A Summary of Current Program, 7/1/65

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and Preliminary Report of Progress

for 7/1/64 to 6/30/65

SOUTHERN UTILIZATION RESEARCH AND

DEVELOPMENT DIVISION

of the

AGRICULTURAL RESEARCH SERVICE

UNITED STATES DEPARTMENT OF AGRICULTURE

and related work of the

STATE AGRICULTURAL EXPERIMENT STATIONS

This progress report of U.S.D.A. and cooperative research is primarily a tool for use of scientists and administrators in program coordination, development and evaluation; and for use of advisory committees in program review and development of recommendations for future research programs.

The summaries of progress on U.S.D.A. and cooperative research include some tentative results that have not been tested sufficiently to justify general release. Such findings, when adequately confirmed, will be released promptly through established channels. Because of this, the report is not intended for publication and should not be referred to in literature citations. Copies are distributed only to members of Department staff, advisory committee members and others having a special interest in the development of public agricultural research programs.

This report also includes a list of publications reporting results of U.S.D.A. and cooperative research issued between July 1, 1964 and June 30, 1965. Current agricultural research findings are also published in the monthly U.S.D.A. publication, Agricultural Research. This progress report was compiled in the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, New Orleans 70124, Louisiana.

UNITED STATES DEPARTMENT OF AGRICULTURE
Washington, D. C.
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INTRODUCTION

The program of the Southern Utilization Research and Development Division is an organized effort through science and technology to increase present uses and to discover and develop varied new uses for Southern farm crops. Our farmers need new markets and strengthened demand for their production. At the same time, the Nation needs the new and better products that science can create from agricultural materials. To this end the Division has been conducting research on cotton, cottonseed, peanuts, tung fruit, citrus and subtropical fruits, peaches, rice, sugarcane, pine gum, replacement crops, sweetpotatoes, cucumbers and other vegetables. The in-house research effort on tung, new oilseed crops, and sugarcane was terminated as of the end of the fiscal year.

The Division's program includes basic and applied research in the physical and biological sciences and engineering. Basic research plays a key role in uncovering new information that may be later exploited in applied research and development. When appropriate, engineers carry out pilot-plant studies of promising laboratory developments to provide engineering and cost data essential to industrial application feasibility determinations. The Southern Division has a total staff of about 540 and the in-house scientific effort in its research program amounts to approximately 275 professional man-years. The Division consists of two Pioneering Research Laboratories (Seed Protein and Plant Fibers), eight commodity-oriented Laboratories (Cotton Finishes, Cotton Chemical Reactions, Cotton Mechanical, Cotton Physical Properties, Oilseed Crops, Food Crops, Fruit and Vegetable Products, and Naval Stores), and one Laboratory (Engineering and Development) for engineering research and development. Headquarters of the Southern Division are located at the Southern Regional Research Laboratory, New Orleans, Louisiana. The Division also has personnel and laboratory facilities at Winter Haven and Olustee, Florida; Weslaco, Texas; Raleigh, North Carolina; and Natick, Massachusetts.

Division scientists consult with specialists from other organizations during both the planning and the execution of the research, and cooperate actively with industry to facilitate commercialization and utilization of new findings. Much of the cooperation is informal, but some work is conducted under conditions described in written cooperative agreements and memorandums of understanding. Currently 65 such agreements are in effect.

The farm products with which the Southern Division deals not only provide food, clothing and industrial raw materials, but also contribute to the Nation's general prosperity and well-being. Cotton, the Nation's number one cash crop, has an annual farm value of about $2.5 billion. The retail value of cotton products is almost $17 billion. Cottonseed, a byproduct of cotton, has a farm value of around $300 million. The retail value of its products is about $1.8 billion. Citrus grown in the U. S. has a farm value of over $550 million; vegetables over $1 billion; peanuts almost $250 million; rice

about $360 million; and gum naval stores about $30 million. Industries processing these agricultural crops play a vital role in the Nation's economy; agri-business today is about 30% of the Nation's total economy.

There is an urgent need to maintain the traditional food, feed and industrial outlets for agricultural products and to create new and larger markets for them. Utilization research is needed to solve existing problems, to permit adjustment to important trends and to develop entirely novel operations. The opportunities are great and, as shown by past experience, the ability of utilization research to benefit the economy is tremendous. Following are a few examples of significant developments based on the research of scientists at the Southern Division.

Superior Wash-Wear Finishes Adopted by Industry to Enhance the Competitive Position of Cotton. Carbamate wash-wear finishing agents, developed by Department research scientists, are being produced commercially in the U. S. and abroad. These agents are currently used to treat an estimated one million yards of cotton fabric per day. The carbamates produce high-quality wash-wear finishes with outstanding durability to damage by laundering and chlorine bleaching. In addition to retention of smart appearance, the superior durability prevents garment shrinkage after a few launderings as sometimes occurs with cottons treated with less resistant finishes. Research has indicated that superior lightfastness of dyed fabrics can be achieved by the use of carbamate agents with modified alkyl groups. One such agent, dimethylol hydroxyethyl carbamate, shows promise for quick commercialization. In addition to being attractive for manufacturing conventional wash-wear products, this carbamate appears to be a good agent for deferred cure finishing to produce durably creased, wash-wear cotton garments. Moreover, this new agent is readily available and potentially inexpensive. Representatives of three large industrial manufacturers have stated that the cost of carbamate intermediates used in preparation of these wash-wear finishes can be reduced to make the new agents competitive with all but the cheapest wash-wear agents.

Industry Adopts New Zirconium-Copper Treatment to Improve Service Life of Outdoor Cotton Fabrics. In cooperation with the Canvas Products Association International and the Foundation for Cotton Research and Education (affiliated with the National Cotton Council of America) Department scientists recently developed an efficient, inexpensive treatment based on new zirconium-copper antimicrobial agents for improving cotton fabric's resistance to weather and rot. The discovery of a method of solubilizing various inexpensive fungicides (such as copper borate) with zirconyl acetate and zirconyl ammonium carbonate made the new treatment possible. The new agents, all the components of which are commercially available, have the advantages of good resistance to microorganisms such as mildew and algae, good durability, low cost, no odor, and ease of application. More than thirty companies have expressed interest in the discovery, and five of these are currently using the new treatment for commercial production of outdoor weatherable cotton fabrics. Cotton duck

finished with this treatment has completely resisted mildew and algae growth for more than 36 months of outdoor exposure. The QM Research and Engineering Command, U. S. Army, Natick, Mass., has reported that recently completed preliminary tests by an independent testing company indicate that the finish is superior to any other commercially available additive-type fungicide. The major potential for these new antimicrobial agents is for tarpaulins, shoe linings, boat covers, industrial thread, awnings, and tobacco shade cloth. The market potential is estimated to be equivalent to 265,000 bales of cotton per year.

Progress Made in Research on Aflatoxin in Peanuts and Cottonseed. Contamination with aflatoxin is potentially a problem for many agricultural commodities. Significant progress toward controlling this contamination has been achieved by Department research, much of which presently concerns peanuts and cottonseed. An essential first step was the development of efficient methods of assay. Faster, more accurate, and more sensitive procedures have been devised for analysis of peanut and cottonseed products. In fact, a new micro method permits assay of even a small part of a peanut kernel. A working standard prepared by Department scientists and distributed widely to laboratories requesting it has greatly improved standardization of results. Cooperative feeding tests are being conducted on several farm and experimental animals to determine the relation of aflatoxin to adverse physiological effects and to assess the possibility of its transmission in food products. Several important methods of inactivation or removal of aflatoxin have been developed. The acetone-hexane-water mixed solvent developed to remove gossypol also removes aflatoxin from cottonseed during processing, and other low-cost solvent mixtures have also proved effective. Chemical treatments, particularly those based on ammonia, appear to be promising. Finally, limiting environmental conditions for the elaboration of aflatoxin are being defined to prevent or at least minimize its occurrence in these commodities. The research of Department scientists is being conducted in close cooperation with the Food and Drug Administration of the Department of Health, Education, and Welfare, industry groups, academic research centers, and others to ensure the safety of agricultural products marketed for use in foods and feeds.

New Fire-Retardant Paints Based on Tung Oil Offer Improved Market Potential and Protection for the Consumer. Major progress has been made by Department scientists in the development of water-resistant, intumescing, fire-retardant coatings based on tung oil and its derivatives, research conducted with the cooperation and support of the U. S. Army Engineer Research and Development Laboratories and the Pan American Tung Research and Development League. Although fire-retardant paints are available commercially, they are unsuitable for many domestic, industrial, and military uses, since they lack some requisite conventional properties, such as water resistance, and thus cannot be applied to exteriors. In the Department research, vehicles containing tung oil or chemically modified tung oil have been synthesized and formulated into fire-retardant paints. Some of these experimental coatings are highly

resistant to water and to weather and have superior color and color retention, good drying and bonding characteristics, and other excellent conventional properties. They perform well in the standard Underwriters' Laboratories' 25-foot tunnel furnace. The tremendous industrial interest in the formulations indicates that commercialization would help consume large volumes of domestic vegetable oils--not only tung, which is an essential component, but also linseed oil, dehydrated castor oil, and others. However, the research has even more important implications, since effective fire-retardant coatings should greatly reduce losses due to fires: over 11,000 lives and over one and one-half billion dollars' worth of property annually in the United States alone.

AREA NO. 1 - COTTON - BASIC AND EXPLORATORY INVESTIGATIONS

Problem. Cotton, the nation's most important fiber, is facing severe and increasing competition from synthetic fibers. Cotton is America's largest source of cash farm income and still accounts for more than half of the total U. S. mill consumption of all major fibers. However, its proportionate share of the market has been slowly decreasing as has the per capita consumption. The rapid growth of the synthetics at the expense of the natural fibers has been a phenomenon of the century. Expansion of market outlets for the chemical fibers has been based on vigorous research and development programs. The engineering and development programs of the chemical fiber industry are designed to capitalize on the special properties of each individual fiber as related to the functional use qualities desired in particular products; basically they involve the substitution of the newer fibers for cotton in cotton's traditional end-use markets. Expanded research to increase the utilization potential of cotton offers the most realistic opportunity for improving cotton's competitive strength as a textile fiber and for increasing cotton consumption. Basic and exploratory investigations, studies on interrelations among fiber, yarn, and fabric properties, new and improved textile machinery, improvement of wash-wear properties and improved cotton properties and products are basic to holding existing markets or expanding the use of cotton in new applications.

Fundamental information is badly needed in applied research to help cotton gain new and maintain old markets. Fundamental knowledge of the cotton fiber as to its structure, properties, and the mechanisms involved in chemical and physical behavior serves as a basis and a guide in the design and improvement of processing machinery, mechanical and chemical processes, and in the development of new and improved cotton yarns, fabrics, finishes, and treatments. Many chemical and physical treatments, as well as textile organizations and machine designs, offer a basis for the improvement of cotton quality or lowering of processing costs. Exploratory chemical and physical research is needed to determine the true potential of such approaches prior to undertaking extensive developmental research or the construction of prototype machinery. Specific areas in which basic information is needed include the chemical properties and structure of native and modified cottons; the chemical modification of cotton cellulose; chemical reactions induced in cotton cellulose by high energy radiation; reaction mechanisms, rates, and catalysis of cotton cellulose reactions; new concepts and methods for evaluating the physical properties of native and modified cottons; relationships of the structural arrangements within cotton fibers to the physical properties of native and modified cottons; mechanisms of physical damage to cotton due to mechanical, chemical, or biological actions; fine structural changes occurring during chemical and physical modification of cotton cellulose; and correlations of the fine structure of cotton fibers with their gross behavior in textile structures.

USDA AND COOPERATIVE PROGRAM

The Department has a continuing long-term program involving organic chemists, analytical chemists, physical chemists, physicists, microscopists, chemical engineers, statisticians, mathematicians, cotton technologists and textile technologists engaged in basic and exploratory studies to develop fundamental information needed in applied research to help cotton gain new and maintain old markets.

Basic research on the structure of cotton fiber and its relation to the behavior in mechanical and chemical treatments, essential to an understanding of the performance of fibers during processing and in textile products, is carried out at the Southern Regional Research Laboratory, New Orleans, Louisiana. Included is the research of the Plant Fibers Pioneering Research Laboratory to obtain basic information on the supermolecular structure of plant textile fibers; and to relate information of polymer and fiber structure to the mechanical and textile behavior of fibers. Additional basic research on chemical and physical properties and structure of cotton is being carried out: (1) under contract at Stanford Research Institute, South Pasadena, California, on determination of the structural components of the cotton fiber that contribute most to tensile strength and how they can be utilized to increase tensile and recovery properties; at Texas Agricultural Experiment Station, College Station, Texas, on the effect of variation in structure on cotton fiber properties caused by environmental and genetic factors; at the University of Tennessee, Knoxville, Tennessee, on investigations to determine the effects of fiber extensibility on fiber breakage in mechanical processing; at the Polytechnic Institute of Brooklyn, Brooklyn, N. Y., on relationship of molecular size, nature, shape, conformation, and configuration of organic non-aqueous compounds to their swelling power on cotton cellulose; and at Harris Research Laboratories, Inc., Washington, D. C., on investigation of factors influencing comfort in cotton apparel fabrics; and (2) under grants at Massachusetts Institute of Technology, Cambridge, Massachusetts, on investigation of fiber and yarn geometry in areas of deformation in cotton fabrics; and at Georgia Tech Research Institute, Atlanta, Georgia, on elucidation of the role of fiber morphology on frictional behavior.

Exploratory chemical and physical research is also conducted at New Orleans, Louisiana, as a basis for the improvement of mechanical and chemical processing, and in the development of new and improved yarns, fabrics, finishes, and treatments. One phase of the research -- exploratory investigation of reversible chemical reactions to obtain information basic to the development of a commercially feasible reversible crosslink -- is conducted with cooperation and support by the Cotton Producers Institute. The International Lead Zinc Research Organization cooperates in and supports exploratory research to impart useful properties to cotton through application of lead, zinc, and other metal compounds. Additional exploratory chemical and physical investigations are also being carried out: (1) under contract at Macrosonics Corporation, Carteret, New Jersey, on

treatment of cotton fibers with acoustic energy; at Gagliardi Research Corporation, East Greenwich, Rhode Island, on chemical modification of cotton through treatments with reagents in the vapor phase; at Harris Research Laboratories, Inc., Washington, D. C., on the development of finishes for cotton fabrics to render them more rapid drying; and (2) under a grant at Textile Research Institute, Princeton, New Jersey, on crosslinking of chemically modified cotton to obtain cotton fabrics with an optimum combination of resilience and thermoplasticity.

Other research on chemical and physical properties and structure of cotton is in progress under grants of P. L. 480 funds to the following foreign institutions: National Institute of Applied Chemical Research, Paris, France, for a fundamental study of the relation of crystallinity to accessibility in cottons (project duration - 5 yrs.); Swedish Institute for Textile Research, Gothenburg, Sweden, for an investigation of setting reactions in cotton fabrics (project duration - 5 yrs.); Central Laboratory, T.N.O., Delft, Holland, for a fundamental study of the response of cotton fiber structural elements to stress (project duration - 3 yrs.); Fiber Research Institute, T.N.O., Delft, Holland, for an investigation of the fundamental mechanisms and bonding forces that could be used to improve tensile strength and other physical properties of cotton textiles (project duration - 5 yrs.); Ahmedabad Textile Industry's Research Association, Navrangpura, Ahmedabad, India, for a study of the relation between the fine structure and mechanical properties of cotton fibers by swelling and stretching treatments (project duration - 5 yrs.); and for a study of the physical chemistry and thermodynamics of solution and vapor phase adsorption on and in the cotton fiber (project duration - 5 yrs.); University of Bombay, Bombay, India, for an investigation of the photochemical degradation of cotton (project duration - 5 yrs.); and for an investigation of new solvents for molecular weight determination of cellulose (project duration - 3 yrs.); Indian Central Cotton Committee, Bombay, India, for investigation of the microbial decomposition of cellulose with special reference to the effect of Indian bacterial organisms on cotton and cotton fabrics (project duration - 4 yrs.); Juan de la Cierva School of Technical Investigations, Barcelona, Spain, for a study of the measurement of "total hairiness" of cotton yarn and the determination of mechanical factors contributing toward its formation (project duration - 5 yrs.); The Cotton Silk and Man-Made Fibres Research Association, Shirley Institute, Didsbury, Manchester, England, for a study of the effect of swelling agents on the fine structure of cotton (project duration - 5 yrs.), and for an investigation of chemical modifications of cotton fabrics involving control of lateral molecular order and distribution of crosslinks (project duration - 3 yrs.); Shri Ram Institute for Industrial Research, Delhi, India, for a fundamental investigation of moisture sorption and desorption by variously crosslinked cotton celluloses over the entire humidity range (project duration - 5 yrs.); State University of Ghent, Ghent, Belgium, for a fundamental study of the nature and origin of reversals in cotton fibers and their relation to mechanical properties of the fibers (project duration - 4 yrs.); and Swiss Federal Institute of Technology, Zurich, Switzerland, for a study of the chemistry and structural nature of

the bonds formed between formaldehyde and cellulose in formaldehyde-treated cottons (project duration - 5 yrs.).

Exploratory chemical and physical investigations are in progress under grants of P. L. 480 funds to the following foreign institutions: Birkbeck College of University of London, London, England, for a fundamental study of the preparation and properties of phosphazene and phosphoryl chloride derivatives having potential for reaction with cotton cellulose (project duration - 4 yrs.); The Hebrew University of Jerusalem, Jerusalem, Israel, for the synthesis and determination of properties of new aziridinyl phosphorus compounds having potential for use in the treatment of cotton (project duration - 3 yrs.); Indian Central Cotton Committee, Bombay, India, for an investigation of the preparation of radioresistant and radiosensitive celluloses (project duration - 5 yrs.); Ministry of Commerce and Industry of State of Israel, Jerusalem, Israel, for a fundamental study of the oxidation of cotton and crosslinked cotton by various oxidizing agents (project duration - 3 yrs.), Chalmers University of Technology, Gothenburg, Sweden, for a basic investigation of the behavior of cotton subjected to aerodynamic forces (project duration - 3 yrs.); and Shri Ram Institute for Industrial Research, Delhi, for a fundamental investigation of heat and mass transfer rates in the drying and curing of resin-treated cotton textiles by counter-current solid-gas contact systems (project duration - 5 yrs.).

The Federal in-house scientific effort devoted to research in this area totals 60.1 professional man-years. Of this number 35.7 is devoted to chemical and physical properties and structure and 24.4 to exploratory chemical and physical investigations. The domestic contract and grant research involves an additional 14.9 man-years, 10.0 being on chemical and physical properties and structure, and 4.9 on exploratory chemical and physical investigations. P. L. 480 research involves 21 grants, of which 15 are on chemical and physical properties and structure and 6 on exploratory chemical and physical investigations.

The following lines of work were terminated during the year: (1) Development of improved instrumental techniques for selected elemental analysis of additively and chemically modified cottons to aid in improvement of cotton textile products; (2) Fundamental investigation of crimp in cotton fibers and its relationship to other fiber properties, as well as its effect on processing performance and product quality (P. L. 480 project), (under Chemical and Physical Properties and Structure); (3) Exploratory investigation of the reaction of acetylene and related compounds with cotton cellulose (under Exploratory Chemical and Physical Investigations).

PROGRAM OF STATE EXPERIMENT STATIONS

Station research on cotton and cotton fiber utilization is directed to a number of application studies evaluating mechanical harvesting, ginning processes, and textile properties.

The influence of mechanical harvesting factors is being studied by several stations in the cotton belt. Two of these investigations relate to fiber quality and moisture content of seed cotton at the time of harvest. The extent of mechanically harvested foreign matter inclusions and composition of foreign matter have been subjects of interest for both the machine design and the gin operation. High speed motion pictures of harvesting action have served as a research aid in studying spindle action and elimination of foreign matter pick-up. It has been demonstrated that moisture vapor transport from trash to very dry field cotton results in a desirable water-tempering effect leading to improved ginning material which retains good staple length and, hence, fibers with better spinning potential. Evaluation of chemical agents as preharvest defoliants, controlants of weeds, cotton preservatives, and for fungicidal-moistening action on harvester spindles continues. In a study directed toward the development of new principles and techniques for ginning cotton, the use of electrostatic fields to remove and recover fly lint from gin exhausts is under investigation.

A program of research to develop improved instruments for measuring fiber characteristics such as length, fineness, maturity, tenacity, elongation, crimp, and compressibility is continuing. It is directed to provide convenient devices of precision for plant breeders measuring physical properties of small samples.

Knowledge of cotton plant growth is being developed to understand the transport of oxygen from air-permeated soils to germinated seedlings and the route of water vapor transport during emergence. Other studies include the catalytic behavior of trace metals such as molybdenum and manganese in cotton plant metabolism. The function of auxin in ethylene biosynthesis is inhibited by the presence in cotton of yet unknown water-soluble compounds containing phenolic groups. The toxic role of manganese as a co-factor in this reaction has been demonstrated in continuing studies of indoleacetic acid-oxidases. Disease resistance and susceptibility of cotton to xanthomonads has been associated with molybdenum nutrition of the plants and a study of amino acid patterns is being pursued to provide laboratory indicators of resistant and susceptible strains.

Three regional studies are directed to determining: (1) the mechanism of fabric stress absorption and performance; (2) the relation of fiber properties to end-product performance (cotton sheets); (3) properties of drapery and upholstery textiles and their importance to consumer satisfaction.

Other workers are conducting similar use tests of cotton garments and evaluating physical and chemical properties of fibers and fabric finishes.

A total of 13.7 professional man-years is devoted to this research.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical and Physical Properties and Structure

1. Fundamental Investigations of Adsorption and Swelling Phenomena in Native and Modified Cottons. Microscopical investigations of absorption phenomena in native, mercerized, and modified cottons have continued. Preliminary experiments have been conducted on the use of lead acetate for electron staining of raw, scoured, slack and tensioned-mercerized fibers, and fibers from fabrics treated to different levels of crosslinking with formaldehyde. It has been demonstrated that lead, in the form of particles, is deposited in spaces within the fibers, but no definite correlation between particle size and radial structure has yet been made. Further studies of absorption by revised electron staining techniques will be carried out and the data correlated with that obtained via adsorption of nitrogen at liquid nitrogen temperatures in order to delineate differences in fiber microstructure of selected types of modified cottons. If feasible, similar observations of cottons swollen in various solvents will be made by the same techniques. (S2 1-209, S2 1-209(Rev.)).

In research to determine the properties and structural characteristics of cotton fibers which influence the capacity of the fibers to sorb alkaline solution, effort is being directed toward establishment of optimum conditions for the alkali swelling centrifuge test. Preliminary experiments have indicated that changing details of the test, such as duration of mechanical shaking and percentage of wetting agent employed, influences alkali centrifuge values (ACV) both in level and in variability. It was found that a 3.5-unit decrease in ACV resulted for each unit increase in moisture content of the conditioned specimens; this is due to the mathematical relationship rather than to a change in sorptive capacity of the cotton fibers. Specimens unduly exposed to lower atmospheric moisture conditions after removal from the centrifuge had lowered ACV's, presumably due to loss of moisture to the atmosphere. The effect of centrifugation time apparently varies with the morphology of the fibers. Also, ACV is influenced by the percentage of sodium hydroxide in the soaking solution. These test variables will be investigated further. Additional ACV data on intracard specimens confirmed again the usefulness of the ACV test in investigating the possibly deteriorative actions of components of processing machinery, as indicated by increased ACV's. (S2 1-249).

Basic studies of the relationship of molecular parameters of organic compounds to their swelling power on cotton cellulose have been initiated in contract research at the Polytechnic Institute of Brooklyn. It has been shown that use of the differential dyeing technique may not give a valid measure of the swelling of cotton. A differential scanning calorimeter has been installed and calibrated; it will be used for detecting heat changes during the swelling of cotton in selected nonaqueous media. Some progress has been made on the use of microscopical techniques to measure cross-sectional areas of swollen cottons and to follow changes in fiber dimensions

with swelling in nonaqueous media. Correlation of heat changes with changes in fiber dimensions should aid in the elucidation of the phenomena involved in the swelling of cotton. (S2 1-225(C)).

2. Basic Studies of the Relationships of the Structural Arrangements Within Cotton Fibers to the Physical Properties of Native and Modified Cottons. Microscopical techniques have been applied to various types of chemically modified cottons to observe differences in fiber structure. In investigations of crosslinking mechanisms, microscopical comparison of products of divinyl sulfone and of bis(hydroxyethyl)sulfone treatments indicated that both of these treatments had produced fibers well enough crosslinked that no layer separation could be induced by the layer-expansion specimen preparation technique. Preliminary exploratory investigations of the reforming of broken crosslinks in samples treated with the reactive dye "Remazol G" (sulfone crosslinking agent), and subsequently reduced by zinc hydrosulfite, indicated that diazotization followed by treatment with coupling agents could be followed microscopically by the layer-expansion technique and by swelling of the cross sections in cupriethylenediamine. In the experiments tried, neither H-acid, nor chromotropic acid reformed the crosslinks, but resorcinol did. Dialdehyde cotton showed distinct layers, comparable to those found for untreated cotton, when sections were embedded wet in methacrylate; however, crosslinking dialdehyde cotton with carbohydrazide gave a product in which the majority of fibers showed no layer separation by the layer-expansion technique. Observations of cotton fibers grafted with polymethyl methacrylate and polyacrylonitrile by postirradiation methods indicated that the fibers are more heavily reacted in the outer regions; whereas, with polyvinyl acetate, reaction occurred more uniformly throughout the whole fiber. Changes in refractive index of cotton fibers mercerized after crosslinking with butadiene diepoxide indicate that post-mercerization does affect birefringence in samples pretreated with 2% sodium hydroxide but not those pretreated in 15% or 23% sodium hydroxide. The former samples showed no change in orientation on aging, but those pretreated with the higher alkali concentrations did exhibit changed refractive indices on aging. Measurement of refractive index may become a useful tool for additional evaluation of chemically modified cottons. Location of areas of graft polymer within the cotton fiber will assist in the interpretation of mechanisms in high energy radiation experiments. (S2 1-263).

In research on the effects of gross and fine structure of cotton fibers on their physical behaviors, the relationships of tenacity to cellulose orientation found in earlier investigations have been substantiated in experiments with another series of American and Asiatic type cottons having a wider range in properties. Toughness (1/2 tenacity x elongation) and crystallite orientation are not linear relationships irrespective of cotton variety; the Pima S-1 type cottons have higher tenacity for comparable orientation than the American upland type. High crystallite orientation in general is related to high cellulose density, a relationship which is more pronounced if water solubles are removed. Experiments where high tension was used during resin treatment of several varieties of cotton in the form of 16/2

low-twist yarn confirm the large effects of tension. High tension may increase the strength of slack mercerized yarn over that of the tension mercerized control, but even low tension is sufficient to restore the strength of slack mercerized, acid degraded yarns to the strength of their controls. Although slack resin treatment does not appreciably change the modulus or stress-strain curve of the slack mercerized, acid degraded yarns, high tension during the resin treatment of these yarns may increase modulus over 24-fold. Tension during resin treatment does not generally affect the toughness. Fibers with structural differences caused by growth conditions and by species will be examined for relationships.

Special cottons grown in growth chambers (see project S2 1-217(C), below) under conditions of constant illumination but varying temperature have been found to develop diurnal growth rings, although no diurnal growth rings developed when temperature was kept constant and light varied. Many properties of the fibers grown in chambers with varying light and temperature as encountered under outside conditions were generally comparable to those of field-grown cotton. Cell walls of fibers grown under constant conditions of temperature, moisture, and illumination, observed with the optical microscope after swelling with cuprammonium hydroxide, disclosed no evidence of a striated structure as found in field-grown cotton. However, when methylmethacrylate, a strong swelling agent, was used to swell the cell walls, the fibers ruptured into similar layers or fragments regardless of growth conditions. Only small differences in strength, elongation, and cellulose orientation were found for cottons with and without growth rings. This further substantiates the observations of comparable basic structure and indicates that the growth ring structure could be relatively unimportant. The spirality of structure and reversals are found in cotton grown under constant conditions. (S2 1-208).

Cottons are being grown in growth chambers under various controlled conditions of temperature, illumination, humidity, etc., by the contractor (Texas Agricultural Experiment Station) for studies of fiber structure differences caused by environmental and genetic factors. Conditions of growth have been found to affect plant development, fiber properties, and the period required to develop the fiber. Environmental effects on the five varieties of cotton investigated were found to vary, the Rex variety being the most consistent producer of developed fibers under the various light-temperature conditions studied. One strain, NR-AHA-C, has shown unsatisfactory response to flower setting and fiber production under the conditions investigated. The diurnal growth ring structure was found in cottons from a temperature fluctuating environment rather than a light fluctuating environment. Various properties of the specially grown cottons are being studied in detail in the aforementioned project, and in the Plant Fibers Pioneering Research Laboratory. (S2 1-217(C)).

Fundamental information concerning fiber components that contribute most to the strength properties of cotton is being developed in contract research at Stanford Research Institute. Although the treatment of cotton yarn with

various types of swelling agents has been found to cause changes in the internal fiber structure, only the swelling agents that are capable of breaking strong hydrogen bonds between the cellulose chains are capable of improving the strength properties. Electron micrographs of the surface and cross section of fibers treated by various types of swelling agents do not indicate structural changes that are associated with strength properties. The conversion of crystalline cellulose I to cellulose II apparently is not necessary to obtain increased molecular orientation by swelling-tensioning treatments. Most of the conversion apparently takes place during washing when sodium hydroxide solutions are used. Swelling of chemically modified cotton that swells only in the regions of modification does not result in improved strength properties on subsequent mechanical stretching. (S2 1-206(C)).

Fundamental studies of the role played by the structural elements of the cotton fiber in response to stress are being conducted in P. L. 480 research at the Central Laboratory, T.N.O. under a project now nearing termination. Through the use of modern microtechniques for manipulating and observing single fibers, a better understanding is being obtained of the internal movements that occur within the cotton fiber while it is being subjected to torsion and stretching. Fibers treated by resin treatments commonly used in wash-wear finishing of cotton have been found to be more rigid to torsion and to begin to form cracks and break at lower torsion than untreated fibers.

Observations of stress concentrations and slip phenomena in native and resin treated fibers are furnishing new data that confirms present views and extend the knowledge of cotton fiber structure and behavior. Such basic knowledge of cotton fibers eventually will be directed toward efforts to improve cotton fiber properties through cotton breeding programs and improvements in cotton processing. (UR-E19-(20)-4).

Research under a P. L. 480 project at the fiber Research Institute, T.N.O., in Holland to investigate the fundamental mechanisms and bonding forces that could be used to improve the tensile strength and other physical properties of cotton textiles is now in its early stages. An excellent survey of current literature in this area of research has been made. Work is now underway to determine the physical and mechanical properties of combed yarns after treatment with various media that strongly swell cotton fibers. Information growing out of research under this project is expected to be useful in improving processing treatments to yield cotton fabrics having improved strength characteristics. (UR-E19-(20)-12).

In P. L. 480 research at the Swedish Institute for Textile Research, reactions which will cause setting in cotton fabrics and garments are being investigated. Treatment of cotton fabrics with solutions of certain inexpensive alkalis or inorganic salts which cause swelling of the cotton fibers has been shown to cause the relaxation of internal stresses in the fabrics. This treatment, which is generally known as "setting," decreases surface mussiness of the fabric, and in combination with standard resin

treatments, results in improved wash-wear properties. It has been observed that the conditions under which deswelling of the fibers occur during treatment greatly influence the "setting" effect. More recently, a study has been made of the "setting" effect, when used alone, of inorganic salts that are used as catalysts in resin treatment of fabrics. Setting determinations have also been conducted under condition of time, temperature and concentration similar to those employed in industrial finishing, such as mercerizing, kier boiling and bleaching, to obtain a better understanding of these processes from the point of view of "settings". Information developed is expected to assist in providing the basis for reducing the amount of resin required to provide acceptable wash-wear qualities in cotton textiles. (UR-E26-(20)-2).

3. Elucidation of Mechanisms of Physical Damage to Cotton Due to Mechanical, Chemical, Physical or Biological Actions. Investigations to determine the effects of fiber extensibility on fiber breakage in mechanical processing have been initiated under contract at the University of Tennessee. Initial techniques developed and investigated for possible application in determining differences in fibers related to fiber extensibility or ease of breakage in processing involved the crushing of fibers with known forces, and determination of torsional properties of the fibers before and after crushing. The research has shown that the magnitude of differences in fiber geometry is sufficiently large that changes in structure estimated from changes in torsional rigidity should be determined on the individual fibers before and after the structure change rather than on fibers randomly selected from the bulk samples. Since the torsional property changes resulting from crushing single fibers are dependent upon both the changes in fiber geometry and the fiber damage, use of the individual-fiber test approach for determining torsional changes on the crushed fibers is not informative. The most reproducible method found thus far for determining resistance to crushing as indicative of brittleness is the application of pressure to a plug of cotton fibers. Techniques for measuring density, torsional rigidity, and moisture regains as indicative of changes in fiber structure have been standardized and the statistical reliability established. (S2 1-221(C)).

An investigation of the photochemical breakdown of cotton under different conditions of exposure to radiation is being continued in P. L. 480 research in India at the University of Bombay. It is well known that cotton fabrics are weakened by prolonged exposure to sunlight or to strong illumination. Progress is being made toward determining the mechanisms by which photosensitization and photolytic degradation of cotton and selected modified cottons take place. Photodegradation has been shown to proceed by random chain scission, the course of which is represented by two stages, each obeying first order kinetics, the initial stage proceeding at a faster rate of reaction than during the subsequent stage. The role of moisture in photochemical degradation of cotton and modified cottons has been clarified. Basic knowledge of this type is expected to be useful in devising practical means to prevent the deterioration of exposed cotton fabrics by means

of chemical inhibitors or screening agents that prevent or interfere with the sequence of reactions involved. (UR-A7-(20)-4).

Under a P. L. 480 grant at the University of Bombay, a study is being made of new, more stable solvent systems for cellulose in the determination of the average molecular weight of cellulose by the disperse viscosity technique. Copper complex solvent systems widely used for this purpose are highly colored and are extremely oxygen-sensitive, factors which greatly complicates their preparation, storage, and use. Substantial progress is being made in studies of several iron tartrate and cadmium ethylenediamine complex solvents that are relatively colorless and insensitive to atmospheric oxygen, and in relating data obtained with them to comparable data with the older copper complex systems. Means have been developed to apply a two-component solvent system to the dissolution of high degree of polymerization cottons and mercerized samples that are difficult to dissolve in the usual solvents, thus permitting satisfactory measurement of these materials. Studies have been made of the kinetics of degradation of cellulose solutions at several temperatures and attempts have been made at fractionation in iron tartrate solvents. The information obtained in this project will be useful in following the degradation of cotton by various treatments, through the application of a simplex procedure for intrinsic viscosity measurement. (UR-A7-(20)-30).

4. Investigation of the Structural and Compositional Changes Occurring During Chemical and Physical Modification of Cotton Cellulose. Pioneering research on plant fibers has been pursued along a number of lines by the Plant Fibers Pioneering Research Laboratory. Considerable attention has been given to the crystalline state of various cellulosic materials, chiefly through the use of X-ray diffraction procedures. Three aspects of the crystalline nature of cellulose are under examination. These include (1) the degree of crystallinity, (2) the size of the crystalline regions, and (3) the change in crystal geometry as a result of chemical modification. A new readout system for the X-ray diffractometer has been installed, which will provide punched tape and/or typewritten data as well as potentiometer recorder tracings of diffraction curves.

A method for obtaining the degree of crystallinity of cellulose by point-by-point comparison of diffraction intensities of highly crystalline, highly amorphous, and the experimental material was developed of some years ago under research contract for SU by Wakelin and his associates at Textile Research Institute, Princeton, New Jersey. The method overcomes many of the theoretical objections to X-ray crystallinity measurements, but is rather tedious in the mathematical treatment of the data. To take advantage of the validity of the method, a computer program has been written which employes punched tape data. The computer operations have been carried out on the IBM 1620 computer at the ARS computer center at Beltsville, Maryland. Cottons of the same variety grown in the field and under controlled environmental conditions of light and temperature at the Texas A&M Experiment

Station were examined by the programmed Wakelin technique. Significantly higher crystallinity was found in the field-grown cotton fibers, whereas estimations by the empirical peak intensity measurements had shown relatively little difference.

In the studies of crystallite size by X-ray diffraction procedures, means of avoiding the excessive computations required are under development through use of the punched tape readout system of the diffractometer and computer processing at the computer center at Beltsville, Maryland. The crystallite dimensions of several celluloses have been estimated from measurements of the peak width of the tracings of the (002), ($10\bar{1}$), and (101) interferences. (In each case, these interferences arise from interplanar spacings perpendicular to the chain direction of the cellulose, and therefore represent diameter measurements of the crystallite.) In a given sample, each interference gave approximately the same value for the crystallite diameter. Untreated cotton crystallites had a diameter of approximately 50 Å; this increased to 60 A in cotton cellulose after hydrolysis. Commercial wood hydrocellulose (Avirin) had a diameter of approximately 33 Å. Fourier analysis has not yet been applied to these experiments, but it is hoped that some estimate may be obtained also of the distribution of crystallite sizes which make up the average.

Introduction of ester or ether groups into the cellulose molecule disrupts the interplanar spacings originally present, and brings about new crystalline arrangement of the modified cellulose chains. In a series of derivatives in which the group introduced was relatively large, new interferences were found which arose at the expense of the orignal (101) spacing, and which correspond to much larger interplanar distances. In an extreme case, the menthyl terephthalate ester of cellulose displayed a (101) interplanar spacing of approximately 25 Å - a 240% increase. This is the largest spacing thus far found in chemically modified cotton which still retained useful fiber properties. In general, the lattice distention accompanying chemical modification was found to be proportional to the size of the group introduced, although the position taken up by the group strongly affects the extent of the change. Thus, both benzhydryl (diphenylmethyl) and trityl (triphenylmethyl) cellulose have a smaller interplanar spacing than benzyl (monophenylmethyl) cellulose. This can only arise if the benzene rings of the trityl and benzhydryl groups take up an average position which is relatively flat, i.e., perpendicular to the plane of the anhydroglucose ring of the cellulose chain. In continuing work it is planned to determine the dimensions of the unit cells and the crystallite sizes of the modified celluloses currently under study.

Studies to reveal the extent of development of crystalline cellulose at different stages of growth are being continued. The effects of the environmental factors of light and temperature during fiber growth on the fine structure of the cellulose in the fiber are being examined. Under contract S2 1-217(C) cotton bolls are being grown at Texas A&M University in growth chambers under controlled conditions. The first series of bolls,

grown under continuous illumination and an alternating temperature schedule of 15 hr. at 80°F. and 9 hr. at 70°F., have been received and some preliminiary examination has been made. A second series, grown under continuous light and alternating temperatures of the same intervals at 90°-70°F., have been harvested.

Some tests are under way to compare freeze-drying as opposed to storage in absolute methanol as methods of preservation of fresh or undried fibers. Also, storage in water and solvent-exchange to pentane, with removal of pentane under nonaqueous conditions is being tried.

Studies of the structural organization of cellulose as revealed by kinetics have continued. One phase of this work involving heterogeneous cyanoethylation was completed. The reaction was carried out on fibers saturated with 6% aqueous sodium hydroxide catalyst, by reacting them with liquid acrylonitrile at a preselected temperature for the desired time. The application of Sakurada's equation for a diffusion-controlled chemical reaction and fundamental kinetic laws were considered. The effects of temperature from 31°C.to 60°C.,dilution of the reagent with different organic liquids, reduction of crystallinity prior to reaction, and previous distribution of catalyst in the fiber were considered with respect to their effect on the reaction rate. Sakurada's equation was found to be obeyed approximately at the higher reaction temperatures but deviations were observed at the initial stages. The rate of reaction generally falls abruptly toward the later stages. The position of the sudden change of rate is somewhat dependent on the temperature and was found to be associated with the change of cellulose crystal structure. Approximate energies of activation, calculated from the specific rate constants between 31° and 40°C. and between 45° and 50°C.,were 10.6 and 16.7 kcal., respectively. An empirical relation was found between the constants of Sakurada's equation and correlated with the Arrhenius equation. Energies of activation determined from this relationship were very close to those found in limited ranges by the conventional methods. The mechanism of the reaction is interpreted as a diffusion-controlled process in which hydrogen bond rupture plays a significant role in diffusion.

In connection with a kinetic study of the cyanoethylation of scoured cotton cellulose, it was observed that during the later stages of reaction the product becomes yellow to orange colored and contains considerably more nitrogen than can be accounted for by the simple addition of cyanoethyl groups at each hydroxyl of the anhydroglucose residue. An infrared study has been made of the products at progressive stages of reaction and of certain soluble products and byproducts of the reaction. The infrared absorption spectra of the samples and of the reacted residues show various types of absorption bands characteristic of amino groups. There is also an indication, inferred from a weak band accompanying the nitrile stretching band, of the formation of small quantities of ionic cyanide as a byproduct. At advanced stages of the reaction the broad band in the 1200-950 $cm.^{-1}$ region, characteristic of the cellulosic fiber, largely disapperars leaving only a few weaker bands due to C-N stretching. Comparison was made of the

spectra of the partially cyanoethylated cellulose and the polyacrylonitrile which forms in the stock acrylonitrile, in an effort to characterize the products. It is concluded that the highly cyanoethylated cellulose, partly dissolved in the acrylonitrile, degrades progressively in the presence of alkali and changes through a complex mechanism to various amine derivatives. The yellow to orange color of the highly reacted samples is assumed to be due to these byproducts.

The study of the kinetics of a heterogeneous cellulose propionation reaction has also been completed. Cotton fiber was reacted with propionyl chloride in pyridine. The kinetics of reaction did not obey Sakurada's equation closely and the deviations were more noticeable at lower initial concentrations of the reagent and at lower temperatures. The rate of substitution changed twice during the reaction, the second change being associated with the loss of the cellulose I structure. However, at the final stage of the reaction, when the cellulose I structure was completely lost, the reaction behaved as a first order type. The diffusion equation has been applied in the present reaction by considering that the amount of diffusion of the reagent into the region, which was initially crystalline, would be proportional to the decrease of the cellulose I crystallinity. The mechanism of the reaction in the crystalline and the amorphous regions was examined. It has been concluded that in the crystalline region the hydrogen bond-breaking process has a significant role in governing the reaction.

The effects of chemical modification on the structure and mechanical behavior of plant fibers have also been investigated. Considerable work has been carried out using the pyridine-acyl chloride procedure for the preparation of test-scale quantities of yarns representing different degrees of substitution with ester groups. The Teflon-glass reactor, described in previous reports, was used in the preparation of a series of cellulose 2-ethylhexanoates and of a series of cellulose 3,5,5-trimethylhexanoates. Pyrolytic studies on these esters have shown that at elevated temperatures the ester linkages cleave to yield the free acids. These acids can be separated from cellulose degradation products by gas chromatography. The quantity of acid produced is proportional to the D.S. and can be used to determine the extent of reaction. This finding is important since the esters are strongly resistant to saponification, the procedure ordinarily used to determine the degree of substitution of esters.

The relationship between the configuration of an acid chloride and its ability to react with cellulose has been investigated further using the d, l, and dl forms of monomenthyl terephthaloyl chloride. With these acid chlorides it was found that the reactivities toward cellulose in pyridine fall in the following order: dl > d >> l. The fact that the dl modification is somewhat more reactive than the d form was unexpected and is as yet unexplained.

The stereochemical investigations have been extended to include reactions between cellulose and camphoric acid derivatives. While stable cellulose

esters have been prepared from these derivatives, contradictory data in the literature on the camphoric acid intermediates have complicated the interpretation of the stereochemistry involved. These studies are being continued.

During this period most of the data have been recorded and computed for the effects of benzhydrylation on cotton yarn properties. Substitutions include D.S. (degree of substitution) equal to 0.31, 0.46, 0.87, 1.13 and 1.22. Tensile strength and elongation at break have been determined under standard atmospheric conditions. Tensile strength decreases very slightly (up to 16%) as substitution increases while elongation increases about 75%. The result is that toughness also increases substantially (ca.55%). Due to substantial increases in yarn number (up to 115%) the strength of the yarn, computed as tenacity, decreases about 60%. The density of the fiber substance decreases progressively with substitution from 1.531 g/cc in the control to 1.362 g/cc at D.S. = 1.22, a maximum of 11%. The X-ray diffractograms show that the starting cellulose is incompletely mercerized and that the crystallinity decreases progressively with substitution. The introduction of a small amount of benzhydryl groups (D.S. = 0.31) takes place largely in the residual native crystalline component, leaving a sharp hydrate crystalline pattern. The crystallinity never disappears completely but the beginning of crystalline structure, due to the presence of the benzhydryl group, shows at D.S. = 1.12. Stiffness modulus, and elastic and work recovery have been measured on each substituted yarn and on controls at temperatures from ambient to 225°C. and back again, carried through two complete cycles. In most cases each of the three measures differs strongly during the first heating cycle from the corresponding values during the second heating cycle and both cooling cycles. Evidently, a very fundamental structural change takes place during this first heating cycle. Evidence of second-order transitions are present. The results, thus far, are tentative and analysis and interpretations are proceeding.

A rather detailed study was made of the thermal behavior of samples benzhydrylated to various degrees of substitution from 0.31 to 1.22. Both differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were applied to these samples in helium and air atmospheres. Controls consisted of the original untreated cellulosic yarn and the same subjected to the same media and temperatures in the absence of the reactant (benzhydryl bromide).

In an atmosphere of helium the control cottons showed a small DTA endotherm associated with moisture loss and two well-developed exotherms. The lower begins at about 350°C. after the cellulose has largely volatilized and continues to about 425°C. The second exotherm begins at about 450°C. and disappears suddenly at about 530°C. It is apparently associated with the final stage of the breakdown of the cellulose. Thus, the DTA curves suggest two separate pyrolytic reactions. All of the substituted celluloses in helium show very nearly the same type DTA curves as the controls with two exceptions. No endotherm, due to moisture loss, is seen. And a small endotherm, presumably associated with scission of diphenyl methane, is

superimposed on the initial exotherm at 350-425°C. so that a dip appears there. This endotherm shows little or no change of magnitude related to degree of substitution. The results suggest three successive or overlapping reactions, one requiring energy to initiate, the other two supplying energy.

Interestingly, the pyrolysis of samples in air follows nearly the same pattern as in helium, the principal differences being that the reactions begin at 20-30°C. lower temperature. Again the controls show small endotherms associated with moisture loss and two well-developed exotherms. The lower exotherm again begins after most of the cellulose has volatilized. The introduction of benzhydryl groups into the cellulose leads to the appearance of an endotherm which is superimposed on the initial exotherm of the control samples. Another characteristic feature of the DTA thermograms in air is the much greater magnitude of the exotherm at 450-550°C.; this increases progressively with substitution. There is no evidence that the substituents diphenylmethane, or to a lesser degree, benzophenone, separate from the cellulose at a different temperature from that of the cellulose breakup. Therefore, it must be assumed that they are first liberated as a result of cellulose breakup and do not anticipate the latter or even accelerate it.

A study on the rate of decomposition of cellulose under isothermal conditions has been initiated. Experiments were carried out under helium atmosphere at different temperatures with ball-milled and cut cotton cellulose. The kinetics were followed by determining the weight loss of the material with time at a given temperature. It has been found that after a decomposition of the first 40-50% of the cellulose the reaction behaves as a first order type. The energy of activation was calculated to be 33-37 kcals. The initial reaction on the other hand was found to follow a completely different mechanism which could be treated as a chain reaction. The energy of activation for the initiation of the chain reaction has also been calculated. With cotton cellulose it was about 54 kcals., but with ball-milled cellulose it is much higher than that of the cotton. Infrared spectra of several heat-degraded samples were taken and the absorption bands which developed or were changed have been investigated. The crystallinity index of the samples was determined by infrared technique. X-ray diffractograms of those samples were also obtained. These results are being analyzed in order to get a detailed picture of the mechanism of cellulose pyrolysis. Various proposed reaction mechanisms have been considered and a kinetic equation has been formulated.

A new technique for the application of thermogravimetric analysis to kinetics of pyrolytic reaction has been developed and applied. Theoretically, this is applicable for determining the Arrhenius parameters of reaction order, energy of activation, and frequency factor for each individual reaction in a series of consecutive and simultaneous thermal reactions. Two thermograms are required with different weights of the sample under otherwise similar reaction conditions. The new method is easier mathematically compared to the earlier methods and should supply more information concerning the mechanism of reaction.

Research on crystal lattice changes in fully acetylated cotton has been completed. It was shown by means of gas chromatography, infrared spectra and saponification observations that acetyl groups in acetylated cotton (DS = 2.93) are not replaced by immersion in 72-98% formic acid at 26°C.

Physical chemical studies have been planned which, it is hoped, will help to clarify the nature of the microfibrillar organization of cellulose. Considerable evidence in the recent literature indicates that the matter of the fine structure of cellulosic fibers is far from settled. Based mainly on electron microscope data, these latest postulates envisage folding of the cellulose chain molecule, absence of amorphous structure, elementary microfibril structure instead of fringe-micelle, and the like. Instruments required for the proposed research have been acquired. Included are a Reichert Zetopan research microscope, specially designed precision viscometers, and a Perkin-Elmer Sorptometer. (SU P2).

In other in-house research (not in PF Pioneering Research Laboratory), improved infrared spectral techniques for the study of modified cottons have been developed. Differential infrared spectra of crystalline and decrystalline hydrocellulose I and II have been obtained for the purpose of differentiating the polymorphic forms. Although no new bands have been developed by this technique, there is an advantage in the sharpening of the absorption bands present. The technique of "frustrated multiple internal reflectance" (FMIR) has been successfully applied to obtain infrared spectra of many types of treated cottons. Certain changes in absorption noted in FMIR spectra of the treated samples seem to be surface effects and may possibly result from variations in crystallinity; these differences have not been perceptible by other infrared techniques. Interpretation of these differences may be of use in evaluating molecular structural changes produced by the chemical treatment of cotton cellulose. An additional advantage of the FMIR technique is that spectra can be obtained without changing the physical state of the fabric. In another phase of work, spectra obtained by the KBr disc method on reaction products of several model compounds, including carbohydrates related to cellulose, with DMEU and with formaldehyde, are being interpreted. (S2 1-220).

Development of improved instrumental techniques for elemental analysis of additively and chemically modified cottons has continued. Satisfactory techniques have been devised for quantitative determination of an additional element, silver, in cotton textile materials by the X-ray fluorescence method. Twenty two elements have now been satisfactorily determined by this method. Atomic absorption spectroscopy has proven suitable for determination of potassium at the part per million level. Recent improvements in the method for X-ray fluorescence analysis of cotton textile materials has made it possible to obtain more precise and reliable results. Also, techniques have been developed for accurately determining elements in liquid samples down to 0.05% concentration in some instances. Because of masking by the liquid, this level of analysis is not as low as for solid samples. Correlation of the X-ray fluorescence data with those by atomic absorption will be made. (S2 1-218).

Research has been initiated to investigate the fluorescence spectra of native and modified cotton. A commercial-type spectrophosphorimeter has proven inadequate for the spectrofluorometric examination of solid samples due to the excessive stray light in the monochrometers. An atomic spectrofluorimeter is being procured for use in the research. Extracts of chemically treated cotton batting and modified cellobiose (used as a model compound) have been found to exhibit absorption in the ultraviolet region, which indicates that these samples may exhibit fluorescence when observed with proper instruments. (S2 1-264).

Procedures have been developed for obtaining nuclear magnetic resonance (NMR) spectra of acid hydrolyzates of various treated cotton fabrics and of reaction products of certain crosslinking reagents with model compounds related to cellulose. These spectra may furnish information regarding the location of the hydroxyl functions in these products. The development of new basic information concerning the reactions of cellulose by use of NMR spectroscopy should aid research on the chemical modification of cotton. (S2 1-268).

Research has been initiated to develop new X-ray diffraction techniques for the study of crystalline cotton cellulose and chemically modified cottons in contact with various swelling liquids; and to apply the techniques in a study of the basic factors responsible for swelling. Suitable sample holders have been designed and tested. Preliminary experiments have made it apparent that, in those cases where complex formation does not occur, excess liquid, due to its partial absorption and diffuse scattering of X-rays, will pose a considerable problem in the evaluation of any decrystallization effects on the cotton. Careful adjustment of the sample-to-liquid ratio will be necessary. Also, the relative humidity at which cotton samples are conditioned was found to influence their X-ray diffraction patterns to some extent. (S2 1-276).

Progress is being made in separating and identifying the cleavage products of partially etherified cottons to elucidate the structure of the modified cottons. The identification of 6-O-methylsulfonylethyl glucose as the major substituted glucose formed in the reaction of methyl vinyl sulfone with cotton cellulose has established that the reaction occurs predominantly, if not completely, at the hydroxyl group in the 6-position of the anhydroglucose unit of cellulose. Methyl vinyl sulfone-modified cotton fabrics prepared under a variety of conditions of reaction will be investigated in order to determine the effect of method of preparation on reaction site. The study will then be extended to other chemical agents including crosslinking reagents such as divinyl sulfone. (S2 1-214).

Research to investigate distribution, type, and effectiveness of crosslinks in cotton cellulose by dissolution and swelling techniques is in progress. A reliable and reproducible method has been developed for determination of cupriethylenediamine hydroxide-soluble cellulose in the presence of nonsoluble components. The method has been applied to a series of cottons

treated with a wide variety of di- and polyfunctional agents with interesting results. It is now possible to measure quantitatively the degree to which cotton cellulose is insolubilized by chemical agents in crosslinking treatments. In the case of formaldehyde-modified cottons, it has been found that the level of formaldehyde required for complete insolubility of cotton cellulose in cupriethylenediamine hydroxide varies by more than an order of magnitude from one to another process of reaction. The Form D process conducted in acetic acid stands out in its high requirement of formaldehyde for complete insolubility. The autocatalyzed esterification of cotton with formic acid has been investigated and found to be an effective means for characterizing reactivity or availability for reaction of hydroxyl groups in cotton celluloses modified by various physical and chemical means. Also, an insight into the relative reactivities of the hydroxyl groups has been obtained from a kinetic treatment of the formic acid reaction of a low molecular weight soluble carbohydrate. The specific velocity constant for the primary (No. 6) hydroxyl is approximately double the sum of the velocity constants for the secondary (Nos. 2 and 3) hydroxyls. (S2 1-255).

A fundamental investigation of the effect of swelling and stretching treatments on the fine structure and mechanical properties of cotton fibers is being conducted under a P. L. 480 grant at the Amedabad Textile Industry's Research Association (ATIRA), in India. The effect on fiber fine structure, as revealed by X-ray, microscopic and modulus measurements, of swelling fibers under tension with agents such as solutions of sodium hydroxide, ethylene diamine, and zinc chloride is under study. An instrument technique for measuring the viscoelastic properties of modified cottons has been developed. It has been shown that orientation is considerably more decisive than crystallinity in determining the elastic modulus of cotton fibers. The information being obtained in the investigation is expected to be useful in the selection of treatments to improve the mechanical behavior of cotton products. (UR-A7-(20)-19).

In a P. L. 480 project now nearing its final phases, a basic study of the fine structure of the cotton fiber is being conducted at the National Institute of Applied Chemical Research in Paris, France, to relate fine structure to other fiber properties that are important in the processing and use of cotton. Refined physical and chemical techniques, including X-ray diffraction and microcalorimetry have been applied to the measurement of fine structural features and behaviors of a typical U. S. Cotton of Deltapine variety for which extensive fiber data were available, and to the same cotton treated at several levels of three well-known crosslinking treatments. Extensive data on parameters such as moisture sorption, swelling, crystallinity, and specific surface area have been collected and will be subjected to analysis and interpretation. The information obtained eventually will be translated into the development of improved cotton products. (UR-E9-(20)-61).

A P. L. 480 project is underway at the Shirley Institute, Manchester, England, in which a study will be made of the effect of caustic soda and other swelling agents on the fine structure of cotton. The first phase of the

project, in which a comprehensive and critical survey of of the literature on the swelling of cotton is being made, is now largely completed. This survey will fill an urgent need of researches in the field of swelling and its practical implications in processing and will be made available to them. A record phase of the project, now getting underway, is designed to fill gaps in the literature of swelling made apparent in the survey. (UR-E29-(20)-65).

5. Relationship of Gross Structure of Cotton to Behavior of the Fibers in Textile Structures. A fundamental investigation of the interfiber frictional force and associated fiber properties to improve the processing of cotton products has been successfully completed. Recent work has involved studies of the effects of draft direction and fiber hook removal on processing performance for an extra long staple cotton. In these experiments the cotton was processed into combed and carded yarns using various drafting directions. It was found that when a minimum of fiber hooks trailed into the comber, less noils were removed, better fiber separation occurred, and a more uniform comber sliver was obtained. There were fewer long fibers in the noils and fewer short fibers in the comber sliver. Fiber hooks were reduced to such an extent by the comber and post comber operations that their effect on end breakage and yarn properties was negligible. Generally, drafting with the majority hooks trailing at first and second drawing, leading at roving, and trailing at spinning increased spinning efficiency for carded yarns of the long staple cotton, as was previously found for the short and medium staple cottons. Drafting tenacities of slivers were found to be linearly related to the total amount of fiber hooks. The findings from this research should assist mills in improving their combing and spinning efficiency. (S2 1-201).

Basic research was recently initiated under a grant at Georgia Tech Research Institute to elucidate the role of fiber morphology on frictional behavior important in mechanical processing of cotton fibers and in the behaviors of cotton products. Initial phases of the work will involve a literature survey and the development of techniques for characterizing the surface and morphology of the cotton fiber. (S2 1-248 (Gr)).

Basic investigations of the configurational interactions between fibers and yarns in regions of local deformations in woven cotton textiles have been initiated under a grant at the Massachusetts Institute of Technology. Initial efforts have been concerned with a determination of the extent to which classical engineering concepts can be applied to the bending and unbending of cotton structures. Development of valid engineering concepts and mathematical models to describe the complex movements of cotton fibers in yarns in fabrics during bending and unbending will provide the basis for design and construction of improved textiles for specific uses. Of particular importance in the development of these concepts is the extent to which friction enters into the mechanical distortion of fiber assembles. (S2 1-237 (Gr.)).

A fundamental investigation of fiber crimp, a property possibly responsible

for differences in mechanical processing behavior of cotton fibers, was recently completed under a P. L. 480 grant at the Ministry of Commerce and Industry of the State of Israel. An ingenious apparatus consisting of an optical projection system and a special curve tracer was developed which, used in conjunction with an electronic computer, permitted continuous and dynamic measurements to be made of fiber crimp diameter, considered to be the main crimp parameter of cotton fibers. Using this technique studies were made of crimp in a number of cottons of different physical characteristics on which extensive property data were available. Salient observations were that natural crimp in cotton fibers is a function of fiber size and length rather than a genetical characteristic and is independent of convolutions, reversals in cellulose structure, and crystal orientation angle; fiber crimp tends to be progressively removed in passing through the stages of processing; and cottons of greater crimp tend to behave as shorter, coarser fibers in the spinning process. (UR-A10-(20)-5).

Research is progressing under a P. L. 480 grant at the Juan de la Cierva School of Technical Investigations, Barcelona, Spain, to devise means for the measurement of "total hairiness" of cotton yarns and to determine mechanical factors that contribute to the formation of this phenomenon in the spinning of cotton. It is thought that higher spinning speeds cause increased "hairiness", a fuzzy condition resulting from the protrusion of fiber ends from the body of the yarn. Since for many uses yarns are singed to remove this hairiness, the amount of fibers so removed could have important economic implications. Substantial progress has been made in the development of a prototype apparatus to measure and record the "total hairiness" of cotton yarns employing electronic circuitry. Means to measure this phenomenon is expected to be useful in that it will permit machine adjustments to be made in processing cotton to minimize the formation of hairiness in yarns. (UR-E25-(20)-31).

6. Investigation of Factors Influencing Comfort in Cotton Textiles. The contractor (Harris Research Laboratories, Inc.) has initiated research investigations of factors influencing comfort in cotton apparel fabrics. Experiments conducted in an environmental test chamber have demonstrated the ability of subjects to distinguish differences in sensations of comfort in oxford and broadcloth cotton shirtings under both warm and cool stress conditions, and have permitted selection of physical properties of fabrics which appear to correlate most closely with subjective response. Since it has been found that resin treatment of fabrics for wash-wear finishing, as such, does not reduce the permeability of the fabrics to water vapor, surface properties and thickness-pressure, i. e., structure, relationships appear to be of importance in influencing comfort. A 15-fabric series of shirtings varying in weight, surface characteristics, and resin content have been procured for use in further studies to obtain a better understanding of the factors influencing comfort. (S2 1-241(C)).

B. Exploratory Chemical and Physical Investigations

1. Exploratory Chemical Modification of Cotton Cellulose. The exploratory research project on the crosslinking of various physically modified crystalline forms of cotton has been terminated. Recent work has shown that the use of plied yarn in a fabric is of major importance in the high strength retention during crosslinking afforded by premercerization. Very high breaking and tearing strength retention during wash-wear treatment of cotton fabric was obtained by fabric premercerization at constant dimensions when the fabric was woven of 2-ply yarn of the proper twist. The fabric mercerization at constant dimensions was almost as effective as yarn mercerization and is much simpler. Yarn mercerization at 3% stretch results in high luster along with high strength in the resin-treated fabric. It has been found that the effect of slack mercerization and restretching does not depend on changing the cellulose crystal lattice; reorientation caused by swelling and stretching must be the essential factor. Other experiments, in which yarns were swollen slack and restretched in benzyltrimethylammonium hydroxide and then crosslinked with DMEU, established that neither degree of crystallinity nor degree of accessibility of cotton are factors in determining the strength retained during crosslinking. By contrast, the degree of orientation obtained during restretching of the highly swollen yarns did correlate with the strength retained after crosslinking. (S2 1-210).

In research to develop improved methods of etherifying cotton cellulose, a variety of commercially available polychlorinated hydrocarbons have been successfully used to etherify and crosslink cotton yarn. When applied under alkaline conditions to slack yarn, bis-chloromethyl benzenes and xylenes were found to impart little strength loss to the cotton. Among other agents investigated, hexachlorocyclopentadiene shows particular promise. Yarns treated with this agent had weight gains up to 18-19%, breaking strength retention of 96%, and an elongation at break double that of untreated yarn. A high degree of crease recovery has been obtained by using disulfatomethane salts to etherify cotton to form methylene crosslinks. Relatively small amounts of combined formaldehyde were needed in relation to the crease recovery obtained. N-methylolacrylamide was successfully used in a delayed curing process to produce wash-wear cotton fabrics which under some conditions show considerable resistance to chlorine bleaches. Research on chemically activated cottons as a means of obtaining new cellulose ethers will be conducted. (S2 1-219).

Fundamental investigations of spatial and structural effects of reversible and conventional crosslinks in cotton have been initiated under a new project. An approach for studying the spatial aspects of reversible crosslinking in cotton has been demonstrated. Paired and random placement of crosslinking reaction sites (p-aminophenyl groups) on cotton fabrics was achieved by reaction with a difunctional reactive dye (Remazol Black G) and a monofunctional reactive dye (Rhodazol Yellow 944), respectively, followed by acid reduction of the azo groups in the dyes to remove the chromophoric group. A comparison of the extent of crosslinking on both fabrics after diazotization and coupling (crosslinking) with a bridging reagent showed that the paired reaction sites crosslinked more readily than did those placed in a random

fashion on the cellulose chain. A significant finding was that a variation of only about 10 Angstrom units in crosslink length could be tolerated. Only small changes in wrinkle recovery and other textile properties were noted at the low degrees of substitution achieved. A search for smaller and possibly more reactive reversible crosslinking agents which would effect higher degrees of substitution and more pronounced wrinkle recovery effects will be made. (S2 1-261).

An exploratory investigation of reversible chemical reactions to obtain information basic to the development of a commercially feasible reversible crosslink has been initiated in cooperation with the Cotton Producers Institute. Thermally reversible crosslinking has been related to thermally reversible creasing, the underlying objective of the project. The limits of practical cotton creasing were established as 200°C. for 30 seconds at 0.2 lb./sq. in. iron pressures. A screening method utilizing the Differential Scanning Calorimeter was developed for determining the thermal stability and transition temperature related to linkages chemically attached to cotton cellulose. Thermal stabilities for a series of chemically modified cottons ranged from 160°C. (acetylated) to 344°C. (formaldehyde-treated). An investigation of N-phenyl and substituted N-phenyl carbamylated celluloses showed that electron withdrawing groups on the aromatic nucleus increased the thermal stability of the carbamate linkage and the electron releasing groups decreased the thermal stability. The N-phenyl type having electron releasing groups appears promising since these derivatives have transition temperatures as low as 230°C. Basic information obtained in this research will facilitate the synthesis and development of thermally reversible crosslinks. (S2 1-258).

Exploratory research on the crosslinking of chemically modified cotton to obtain cotton fabrics with an optimum combination of resiliency and thermoplasticity is in progress at the Textile Research Institute under a research grant. Initial work has been concentrated on methods of chemical modification to impart thermoplasticity to cotton and the characterization of the modified cottons. Benzylated and acetylated cottons have been investigated; and benzoylated cotton has been prepared, and reduction of the benzoyl groups to benzyl ether groups is being explored. The research has indicated that the thermoplasticity of chemically modified cottons can be detected and evaluated by use of differential thermal analysis. Gas chromatographic procedures are proving useful for characterization of hydrolysis products of the modified cottons. Crosslinking studies are being initiated. (S2 1-240 (Gr.)).

The major objectives of the fundamental study of reactions between epoxy compounds or their halohydrin precursors and cotton cellulose have been achieved. Basic information concerning mechanisms of ring openings of several diepoxides has been obtained, conditions required for reacting cotton with halohydrin precursors of epoxides have been established, and various types of substituents such as quaternary groups, oleophobic groups, and unsaturated groups have been added to cotton via epoxide reactions.

The research findings should aid in the development of new and improved methods for the chemical modification of cotton to impart desired end-use properties. (S2 1-216).

The contractor (General Aniline and Film Corporation) has completed experimental work in the research on reaction of acetylene and related compounds with cotton cellulose. Vinylated cotton fabrics and yarns of various degrees of substitution (D.S.) were prepared. Above a D.S. of 0.7 severe degradation of the fibers resulted. Discoloration and a slight stiffness were observed in samples vinylated to a D.S. above about 0.3-0.4. Samples with a D.S. of 0.05 and below were found to be soluble in cuprammonium hydroxide solution. Viscosity determinations indicated molecular weights of 43,000 to 137,000 which were considerably lower than the 430,000 molecular weight of the starting cotton. All samples with higher D.S. values were insoluble in the reagent indicating at least a small amount of crosslinking. Most samples had breaking strengths which were 60-85% of that of the controls, and they showed 20-50% elongation-at-break. Further chemical reactions conducted at the vinyl group should result in a variety of interesting modified cottons. (S2 1-199(C)).

In cooperation with the International Lead Zinc Research Organization, research to impart useful properties to cotton through application of lead compounds and other metal compounds has continued. Efforts to scale up the reduction of lead salts to free lead on cotton fabrics were successful. Application of polymeric coatings increased the physical and chemical stability of the finish. The fabrics possessed good rot and flame resistance as well as a high sheen. Optimum conditions have also been established for impregnating cotton fabrics with metallic silver and silver-copper by reduction of ammoniacal solutions of the metal salts with hydrazine and with sodium borohydride. Samples containing up to 50% metallic lead have been obtained without loss in breaking strength; these, in particular, are evoking industrial interest at the present time. However, the silver and silver-copper treated fabrics possess better rot resistance, showing good resistance after four weeks of soil burial, and also have good flame resistance. Cotton fabrics treated with thiomethyl- and thiopropyltriphenyllead have shown good rot resistance after 9 months of soil burial, and those treated with N-(tributylplumbyl) imidazole, triphenyl lead acetate, triphenyl lead laurate, and lead mercaptobenzothiazole are exhibiting good resistance to rot after four weeks of burial. The research will continue along present lines. (S2 1-232).

Recent exploratory work on the chemical modification of cotton fabrics using reagents in the form of fogs or aerosols has involved the spray application of a thermosetting resin to one side of a fabric and a thermoplastic resin to the other side in attempts to enhance the wash-wear properties of the textiles. Some strike-through was noted, but it is believed that the mobility of the treatments can be controlled with thickening agents. The possibility of treating cotton rawstock with wash-wear and other resins for

special properties, then blending these fibers with untreated cotton is also being investigated as a possible means of reducing abrasion damage in resin treated cotton fabrics. (S2 1-247).

Based on exploratory screening experiments by the contractor (Gagliardi Research Corporation), three promising reaction systems for chemical modification of cotton by treatment with reagents in the vapor phase have been selected for more intensive development. Included are: (1) polymerization onto cotton of vapors of chlorosilane monomers, which imparts a high degree of water repellancy through a preferred polymer orientation; (2) the cross-linking with formaldehyde of cottons preimpregnated with urea and other nitrogenous compounds, which yields products having both good wet and dry crease resistance; and (3) graft polymerization onto cotton of the perfluoroacrylates, which imparts oil and water repellancy. These superior functional properties, coupled with better uniformity and lower processing cost, indicate that promising industrial vapor phase techniques can be developed. A prototype vapor phase reactor has been modified for adaptation to new vapor phase reagents, providing for increased flexibility and pointing the way to the requirements of a commercial design. (S2 1-231(C)).

A fundamental study of the preparation and properties of phosphonitrilic and phosphoryl chloride derivatives having potential for reaction with cotton is being conducted under a P. L. 480 grant at Birkbeck College of University of London. The research is an outgrowth of work conducted under P. L. 480 project UR-E29-(20)-35, now expired, under which the chemistry of these interesting inorganic compounds was placed on a sound, systematic basis. Progress is being made in the synthesis, separation, and purification of selected compounds of this type which have configurations that suggest ability to react with cotton cellulose, and in the attachment of cellulose reactive side chains to the phosphazene by replacement of halogens. Interesting compounds have been prepared that possess a high degree of thermal and hydrolytic stability. Polymers containing nitrogen and phosphorus which have good adhesive properties have also been proposed. Fundamental information has been obtained that is useful in understanding the reactions of phosphazene. Certain of the compounds are expected to be useful in the treatment of cotton to afford improved properties, such as flame resistance, ablative and wash-wear properties. (UR-E29-(20)-55).

2. Chemical Reactions Initiated in Cotton Cellulose and Chemically Modified Cotton by High Energy-Radiation, Light, and Heat. Evaluations of the properties of cotton yarns and fabrics grafted with polyvinyl acetate, polyacrylonitrile, and polymethyl methacrylate by the post-irradiation technique have been completed. Vinyl acetate grafting produced marked improvements in flat and flex abrasion resistance of fabrics even at low graft polymer contents. Polyacrylonitrile grafted fabrics did not exhibit marked improvements in abrasion resistance until high vinyl polymer contents were attained ($>25\%$). The polyvinyl acetate-cotton copolymer exhibited the greatest degree of thermoplasticity. The various grafted fabrics retained almost the same strength and elongation properties as the controls. The

grafted yarns exhibited slight decrease in breaking strength, marked increase in elongation-at-break, decreased breaking stress, and marked decreases in average stiffness. Although the weather resistance of the various vinyl-cotton copolymers was not significantly different from that of untreated cotton, polyacrylonitrile-cotton copolymers did exhibit significant resistance to rot in soil burial tests. Radiochemical yields and the rates of the various grafting reactions were determined. With acrylonitrile and methyl methacrylate the grafting reaction occurred predominantly in the outer cellulose layers of the fiber structure, but with vinyl acetate the grafted polymer was uniformly distributed throughout the fiber cross section. Work is presently underway to isolate the vinyl polymers from the cellulose to which they are grafted in order to determine the molecular weights of these vinyl side chains and to relate these findings to the physical properties of the vinyl-cotton copolymers. (S2 1-195).

Electron spin resonance studies of the free radicals produced in cotton cellulose, cellulose derivatives, and various model compounds by heat, high-energy radiation, and ultraviolet radiation have been initiated. Intramolecular transfer of high energy in purified cotton cellulose has been demonstrated to occur over distances several times greater than the length of the "b-axis" of a cellobiose unit. Preliminary results in the research have shown that the substitution of benzoyl, naphthoyl, and benzyl groups on cotton cellulose radiation protects the molecule; also, indications are that substitution of benzoyl groups may increase the weather resistance of cotton. Energy transfer in fibrous cotton cellulose is obviously related to its thermal, photochemical, and radiochemical resistances. It would appear that it may be possible to direct this intramolecular energy transfer to localization in chemically substituted groups from which the energy can be dissipated without cellulose degradation. (S2 1-270).

3. Mechanisms, Rates and Catalysis of Reactions of Cotton Cellulose and of Chemically Modified Cotton. In a fundamental study of mechanisms of cellulose etherifications, rates of reaction between cotton and additional N-methylolurea derivatives currently used commercially in a delayed cure process have been investigated. Effects of catalyst and of time of storage of treated fabrics at various low temperatures (25 to 65°C.) were studied, as well as the effects of N-substituents and C-substituents on the ureas. The research seeks a sound scientific basis for a system which can be used at room temperature for treatment of fabric and which will also permit storage of the treated fabrics under warehouse conditions for long periods of time before use in garment manufacture. Investigation of the chemical kinetics of cellulose etherifications is continuing. (S2 1-196).

Research on the partial esterification of cotton with long-chain monobasic acid chlorides in nonaqueous media has shown that fabrics with high wet and dry crease recovery can be produced by this process even at low levels of esterification (degree of substitution < 0.15). The crease resistance properties imparted to the fabrics vary not only with the chain length of the acid used, but also with substituents and degree of unsaturation in the fatty

acid-moiety. The presence of hydroxyl groups or unsaturation in the fatty acid-moiety improves both the wet and dry crease recovery properties of the finished fabric as compared with cotton fabric finished to a like degree of substitution with a saturated fatty acid chloride of the same chain length. Increase in wet crease recovery angles by presence of unsaturation is even more pronounced than the increase in dry crease recovery angles. These findings are of both theoretical and practical importance. Partial esters of cotton will be prepared by various methods of esterification, and fabric properties of esters of like degree of substitution will be compared. (S2 1-233).

A study of the oxidation of cotton and crosslinked cotton by hypochlorite, hypobromite and other agents commonly used in bleaching cotton products is being conducted at the University of Commerce and Industry of the State of Israel. The P. L. 480 project under which the work is being done is an outgrowth of an earlier project, UR-A10-(20)-4, now completed. Basic information is being developed in early phases of the work concerning the conditions governing the oxidation, degradation and yellowing effects that occur on mild oxidation of cottons treated with crosslinking agents commonly used in the easy-care finishing of cotton fabrics. The information obtained in this research is expected to be useful in improving the characteristics of cottons, especially fabrics treated for easy-care properties for various end uses. (UR-A10-(20)-50).

4. Exploratory Physical Investigations on Cotton. Contract research at Macrosonics Corporation on treatment of cotton fibers with sonic energy is underway. The contractor has designed, constructed, and tested both single and dual face transducer elements for irradiation of cotton samples in liquid media, and has developed analytical instruments for accurate measurement and continuous recording of various operational variables. Preliminary trials were conducted using these transducer elements to irradiate small cotton samples in water with low power acoustic energy over a wide range of frequencies for short periods of time. Under these experimental conditions, negligible effects on moisture regain, tensile strength, and fiber density were noted. However, treatment of larger samples (25 g.) of cotton at two selected frequencies (40 KCS and 800 KCS) for longer times (1 and 1-1/2 hrs.) revealed some small changes with regard to tensile strength, dye absorption, and moisture regain properties. Other fiber properties are currently being investigated. The exploratory research will be expanded to include irradiation in gas media. (S2 1-222(C)).

Under a P. L. 480 project at the Chalmers University of Technology in Gothenburg, Sweden, a basic investigation of the behavior of cotton fibers when subjected to aerodynamic forces is being carried out. Apparatus has been designed which permits the taking of high-speed motion pictures of separated cotton fibers traveling in air streams of different velocities. Conditions and designs are being studied which will cause the fibers to become parallelized through aerodynamic forces exerted by the flowing air stream. Fundamental information of the type being developed in this research is

prerequisite to the design considerations in devising totally new and unorthodox methods for the processing of cotton into useful textile products. (UR-E26-(20)-6).

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AREA NO. 2 - COTTON - INTERRELATIONS AMONG FIBER, YARN, AND FABRIC PROPERTIES

Problem. The intense competition in today's textile markets is placing increasing demands upon cotton producers and processors for high quality products tailored to meet specific use requirements. Improvements in the quality of processed products and lower costs of mechanically processing cotton into yarns and fabrics are needed to satisfy consumer demands and maintain cotton markets. For example, information is needed to determine the effect of the important fiber properties and combination of fiber properties of cottons on yarn and fabric properties and processing performance to obtain the maximum utilization potential from cottons of different fiber properties and to provide guidance for cotton breeders in developing strains having more desirable fiber properties. Improved mechanical processing methods are needed to attain maximum yarn uniformity and the resultant improvements in the general quality level and processing efficiency of all types of cotton products. New and improved methods and instruments for measuring the physical and chemical properties of cotton are needed to guide processing research in developing new and improved products.

USDA AND COOPERATIVE PROGRAM

The Department has a continuing long-term program involving cotton technologists, textile technologists, textile engineers, physicists, statisticians, and mathematicians engaged in research to develop fundamental information and improved processing procedures in order to improve the quality and lower the cost of cotton products during the mechanical processing of cotton fibers into yarns and fabrics.

Research to determine the effect of fiber properties on processing efficiency and product quality is carried out at New Orleans, Louisiana. Additional research of this type is being conducted under contract at Auburn Research Foundation, Inc., Auburn, Alabama: to determine optimum processing procedures for cotton differing in tensile and elastic properties and relate these properties to mechanical processing performance, yarn, and fabric properties. Cooperation is maintained with cotton merchants and textile mills; the Crops Research Division, ARS, and the Cotton Division, C&MS, specially on the procurement of cotton of known history with special fiber properties; and the Market Quality Research Division, ARS, to insure coordination of effort in related research. Research on development of new and improved methods and instruments for measuring the physical and chemical properties of cotton, and evaluating the processing characteristics of cotton, is carried out at New Orleans, Louisiana. Also, contract research is being conducted at Stanford Research Institute, South Pasadena, California, on development of a method for counting neps in cotton at various stages of textile processing; and on development of a research instrument for accurately and automatically determining length, length distribution and diameter of cotton fibers.

Other research on effect of fiber properties on processing efficiency and product quality is in progress under grants of P. L. 480 funds to the following foreign institution: Ahmedabad Textile Industry's Research Association, Navrangpura, Ahmedabad, India, for investigation of means to minimize fiber hooked ends in cotton card and drawing slivers (project duration - 4 yrs.,) and for an investigation of factors affecting drafting in the direct sliver spinning system (project duration - 5 yrs.). Research relating to development of new and improved methods and instruments for measuring physical properties of cotton is in progress under grants of P. L. 480 funds to the following institutions: German Research Institute for Textile Industry, Reutlingen-Stuttgart, West Germany, for the development of an apparatus for counting neps in cotton card web (project duration - 4 yrs.); and Lodz Polytechnic College, Lodz, Poland, for an investigation of the mathematical and theoretical aspects of the relationship between the fiber length distribution of cotton specimens before and after sample preparation (project duration - 3 yrs.).

The Federal in-house scientific effort devoted to research in this area totals 14.5 professional man-years. Of this number 12.6 is devoted to investigations of effect of fiber properties on processing efficiency and product quality and 1.9 to development of new and improved methods and instruments for measuring the physical properties of cotton. The contract research involves an additional 3.9 man-years, 1.1 being on effect of fiber properties on processing efficiency and product quality, and 2.8 on development of new and improved methods and instruments for measuring physical properties of cotton. P. L. 480 research involves 4 grants, of which 2 are on effect of fiber properties on processing efficiency and product quality and 2 on development of new and improved methods and instruments for measuring physical properties of cotton.

The following lines of work were terminated during the year: (1) Large-scale spinning evaluation of the effect of fiber properties and spinning variables on yarn properties and end breakage during spinning; (2) Determination of relationship between the cohesion of cotton fibers and other physical properties of fibers, rovings, and yarns, as a step in improving product quality and processing efficiency (P. L. 480 project) (under Effect of Fiber Properties on Processing Efficiency and Product Quality); and (3) Development of test methods for stretch cotton textiles for use as a guide in producing better cotton stretch yarns and fabrics (under Development of New and Improved Methods and Instruments for Measuring the Physical and Chemical Properties of Cotton).

PROGRAM OF STATE EXPERIMENT STATIONS

(A general program statement is given under Area 1)

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Effect of Fiber Properties on Processing Efficiency and Product Quality

1. Effect of Cotton Fiber Properties Such as Length, Strength, Fineness and Elongation on Fabric Properties and Processing Peformance.

In research to determine the simultaneous effect of pertinent fiber properties and combinations of fiber properties on yarn properties and spinning performance to provide guides for obtaining maximum utilization of cottons of varying fiber properties, the initial investigations on the effect of back drafts, tensor settings, and total drafts on yarn properties and end breakage using the SRRL Accelerated and 720 Spindle Hour Tests have been completed. It was found that end breakage decreased curvilinearly as back draft decreased from 2.7 to 1.3, regardless of total drafts, tensor setting, or yarn number, after which end breakage increased as the back draft was further reduced from 1.3 to 1.02. Generally, a back draft of 1.3 produced yarns of superior yarn strength, elongation and uniformity and minimum end breakage. Evaluations of three major drafting systems have shown that draft distribution is an inherent characteristic of individual drafting systems, each having its own optimum back draft to produce the best combination of end breakage and yarn properties. This finding should be helpful to the textile industry in increasing spinning rates and maintaining yarn quality at acceptable levels. A back draft of 1.3 and a 5 mm. tensor setting have been selected for use in spinning performance evaluations of the 150 experimental cottons accumulated for this research. The cottons have been divided into three groups based on fiber length; the medium length group (1.06" to 1.20") of 79 samples will be processed first using the SRRL 720 Spindle Hour and the Accelerated Spinning Tests. (S2 1-207).

Large-scale spinning evaluations of factors affecting end breakage in spinning have been completed by the contractor (Auburn Research Foundation). The research findings have prompted one manufacturer (the cooperating mill) and probably others unknown to us to place emphasis on blending their cottons on the basis of fiber length distribution, with less emphasis being placed on Micronaire reading or fiber strength. This has led to a better utilization of fiber properties and permitted the use of higher spindle speeds and production with a resultant reduction in the costs of manufacture. (S2 1-178(C)).

In research conducted under a recently completed P. L. 480 project at the Juan de la Cierva School of Technical Investigations, Barcelona, Spain, a study was conducted of the relationships between the cohesion of cotton fibers and other physical properties of fibers, rovings and yarns. The cohesion of cotton fibers affects the roll settings, roll pressures and twists to be used in producing yarns of optimum quality. An improved apparatus was developed for measuring minimum twist of cohesion and through its use the main laws governing the minimum twist of cohesion of cotton rovings and yarns in connection with testing conditions (length and tension) and fiber parameters (length and micronaire) and yarn parameters (number of fibers per cross

section and twist) were determined. It was established that treatments that affect the surface properties of cotton fibers alter the cohesion between fibers and hence the minimum twist of cohesion. This, in turn, affects the settings used in drafting. Information developed in this project should permit the relatively rapid and simple measurement of force of cohesion to be used in predicting the spinning efficiency and yarn properties of cottons of differing fiber properties. (UR-E25-(20)-2).

2. Improved Processing Procedures to Obtain Maximum Utilization of Native and Modified Cottons. Studies of principles and procedures for optimum blending of cottons of varying fiber properties have continued. Relatively large samples of raw stock of three pairs of cottons (low and high short fiber contents, Micronaire readings and fiber bundle strengths) were blended in equal amounts and processed by two respectively different procedures (maximum blending; minimum blending) and spun into yarns. Differences in uniformity between matched pairs of samples (from good mix vs. poor mix) of card, first, and second drawing slivers were too small to permit drawing conclusions. There was a decrease in the quality of yarns--as reflected by measures of length uniformity, gross imperfections, skein strength and variability of skein strength--in the following order for the various schedules of mixes: (1) short fiber content differences (good mix), (2) short fiber content differences (poor mix), (3) Micronaire reading differences (good mix), (4) Micronaire reading differences (poor mix), (5) fiber bundle strength differences (good mix), and (6) fiber bundle strength differences (poor mix). End breakage in spinning increased in the order (1), (3), (5), (2), (4), and (6) of the above listing. This grouped samples from the good mixes as being better than those from the poor mixes. For each of the three aforementioned pairs of blends, one blend was given one picking process, carded, and made into roving; the other was given two picking processes, carded, two drawing processes, and made into roving. Analysis of the appropriate fiber property on sequential lengths of samples showed that the latter "conventional" process--as opposed to the simulated "shortened" process--caused significant deterioration in length and length uniformity and increases in short fiber content; caused increases in Micronaire reading; and produced little, if any, change in fiber bundle tenacity from carding through roving. Elimination of drawing processes as in the "shortened" procedure contributed to lower yarn properties and spinning performance. (S2 1-234).

Contract research was recently initiated at Auburn Research Foundation to determine optimum processing procedures for cotton differing in tensile and elastic properties and relate these properties to mechanical processing performance, yarn, and fabric properties. Based on fiber property tests, the contractor has selected 18 bales of 1-1/16" cotton varying appreciably in strength and representing three levels of fiber-bundle elongation (5.1, 6.8, and 8.5 percent, average) but having comparable fiber lengths and Micronaire readings. Processing tests on these samples have begun. Suitable 15/16" cottons are being collected for the next phase of the research. (S2 1-242(C)).

New research is in progress to determine the effect of high production carding on fiber length distribution and fiber hook formation in card sliver, and to establish improved drafting procedures required for maximum removal of fiber hooks for carded and combed yarns. In preliminary tests with a 1-1/16" Delta cotton, it was found that increases in carding rate caused the amount of trailing (majority) hooks to decrease and leading (minority) hooks to increase. This results in: (1) a net increase in fiber hooks, and (2) a decrease in difference between leading and trailing hooks as production rate increases. This difference between the leading and trailing hooks was generally smaller for low than high cylinder speeds. It was more pronounced for the optimum drafting direction (majority hooks trailing at first and second drawings, leading at roving, and trailing into spinning) than for the conventional direction. The spinning data indicated that the amount of hooks entering spinning and end breakage were highly correlated. Larger-scale processing experiments are in progress. (S2 1-274).

In the spinning of cotton yarns, assemblies of fibers are simultaneously drawn out and twisted. The drafting forces exerted during the spinning operation affect the quality of the resulting cotton yarns. Research has been completed under a P. L. 480 grant at the Juan de la Cierva School of Technical Investigations in which an investigation was made of the effect of various factors in spinning, such as drafting speed, roving twist, apron opening, roll setting, etc., on drafting force in the drafting zones of high draft spinning equipment, and how the drafting forces affected yarn quality. An apparatus was developed for measuring the drafting forces in the front and rear drafting zones. A surprising result of the research was the finding that increases in drafting speed increased the drafting force as well as yarn strength. It was also shown that the parameters that afforded the highest drafting force (without fiber breakage) yield the optimum yarn quality. It was found that with small tensor setting, changes in back draft had less effect on yarn strength and uniformity than with large tensor setting; also tensor setting had less effect on yarn strength as back draft was increased. The investigation provided basic information that will be of assistance in developing improved drafting systems, and in making more efficient use of existing systems. (UR-E25-(20)-13).

An investigation is underway of means to minimize fiber hooked ends in cotton card and drawing slivers under a P. L. 480 project at the Ahmedabad Textile Industry's Research Association in India. Ends breakage in the processing of cotton is related to the presence of hooked ends in the fibers making up sliver. Conventional processing organizations tend to remove hooked ends, but in abridged processes such as direct spinning, the fewer drafting processes between carding and spinning allow more fiber hooks to remain, and hence adversely affect spinning efficiency. Consequently, work under this project is expected to be of use in facilitating direct spinning and improved cotton processing through means to minimize the amount of fiber hooks in card or first drawing sliver. (UR-A7-(20)-51).

B. Development of New and Improved Methods and Instruments for Measuring the Physical and Chemical Properties of Cotton.

1. Development and Adaptation of Instrumental Techniques for Measuring the Changes Imparted to Cotton by Chemical and Mechanical Processes. The research project to develop test methods for stretch cotton textiles has been terminated. Comparison of five different procedures for determining recovery of stretch cotton textiles showed that each method causes a different degree of deformation and, therefore, gives a different value for recovery. The research has shown that in testing stretch fabrics it is desirable to obtain recovery data at several different points of extension. This procedure is necessary to compare fabrics with different stress-strain characteristics and when the end-use is not definitely established. The Static Extension Test, one of the methods investigated in the research, has been reported by others to correlate well with wear tests run on man-made fabrics, but a definite procedure for this test has not been widely adopted. Since the Static Load Test gives somewhat similar results while requiring less material and effort, this test is recommended for evaluating cotton stretch fabrics pending adoption of a standard method. In one phase of the work, a procedure for determining strength, elongation, and recovery of stretch cotton lace was developed. (S2 1-212).

Research to develop more reliable methods of appraising abrasive damage on all-cotton wash-wear fabrics has been initiated. Initial experiments showed that the same type of untreated cotton fabrics which were desized, scoured, and bleached at different times did not exhibit the same flex abrasion resistance. This has been attributed to unequal amounts of residual waxes remaining in the various fabrics after the desizing, scouring, and bleaching steps. Good correlation between flex abrasion resistance and elongation of the fabrics was generally found. However, there appears to be an inverse relationship between flex abrasion resistance and the breaking strength and energy to rupture. Very good correlation between flex abrasion resistance and edge abrasion resistance was obtained when fabrics which had been treated with formaldehyde without use of softeners were tested. The research will continue along present lines. Effects of softeners on abrasion resistance will be investigated. (S2 1-275).

Satisfactory progress is being made by the contractor (Stanford Research Institute) toward development of a method and equipment for rapidly and accurately counting neps at various stages of textile processing. Theoretical evaluations and exploratory research have indicated that the following two approaches appear feasible: (1) a technique based on light scattering by neps and cotton mats, and (2) a technique involving use of colored aerosols for labeling neps. Apparatus has been designed and is under construction for experimental use. The work is being delayed to some extent by difficulty in obtaining delivery of specially made, precision ground lenses and other components for the light scattering unit. (S2 1-229(C)).

P. L. 480 research is continuing at the German Research Institute for Textile Industry to develop an apparatus for the rapid and automatic counting of neps in cotton card web by means of light reflectance and detection. Principles developed through studies using a prototype instrument that scans a sample of card web are now being extended in two promising approaches toward the problem of measuring neps in the running web on the full scale card. The approaches involve the use of some of the principles of television for scanning the web and clever, sophisticated electronic instrumentation has been devised for evaluating these approaches. The development, if successful, is expected to be of great value to cotton processors since it would provide rapid means for following, and perhaps automatically controlling, an important processing variable that affects cotton fabric quality. (UR-E10-(20)-2).

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

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1/ Publication resulting from research under grant of P. L. 480 funds to the foreign institution.

AREA NO. 3 - COTTON - NEW AND IMPROVED TEXTILE MACHINERY

Problem. Blending cotton is an urgent problem in the textile industry now that research has clearly shown the effects of fiber properties on processing efficiency and product quality. Present methods do not permit a homogeneous blend, require excessive floor space and have low production rates. Improvement in carding equipment and procedures is another area in need of research. Due to inadequate methods of feeding, high production cards cannot be utilized to maximum advantage in reducing costs and increasing quality of textile products. The modern cotton mill utilizes ten or more processing stages and, compared to manufacturing systems for competitive products, an excessive amount of labor. The development of a radically new system for processing cotton offers an opportunity for major improvements in strength, uniformity and other functional properties of cotton products, and for substantial savings in manufacturing costs through less damage and waste of spinnable fiber, and through reduction in equipment investment, space and labor.

USDA AND COOPERATIVE PROGRAM

The Department has a continuing long-term program involving mechanical engineers, physicists, and cotton technologists engaged in research to design and develop new and improved equipment for processing cotton into higher quality, lower cost consumer products.

Research to develop improved mechanical processing machinery, for opening through carding, is conducted at New Orleans, Louisiana. This work includes the development of experimental machines and pilot scale machines for evaluation under pilot-plant conditions, and subsequent development of plans for scaling up successful units into practical, commercial size equipment. Current research involves the development of a bale-breaker blender for opening and blending cotton, improved methods of feeding the card, and the development of an improved method and apparatus for removing short fibers and improving fiber parallelization at textile carding machines. Close cooperation is maintained with cotton textile machine manufacturers and cotton textile processors in the establishment and dissemination of engineering specifications for the commercialization of new and modified processing equipment. Additional research in this area is being conducted under contract at General Applied Science Laboratories, Inc., Westbury, L. I., N. Y. on the aerodynamic separation of lint cotton into individualized fibers to provide information needed for improving cotton textile processing equipment.

The Federal in-house scientific effort devoted to research in this area totals 15.4 professional man-years. All of this effort is on the development of improved mechanical processing machinery - opening through carding. The contract research involves an additional 1.1 man-years, in the field of improved mechanical processing machinery-opening through carding.

PROGRAM OF STATE EXPERIMENT STATIONS

(A general program statement is given under Area 1)

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Improved Mechanical Processing Machinery - Opening Through Carding

1. Equipment for Blending Cottons of Different Fiber Properties to Produce Improved Cotton Textiles. Evaluation tests on the pilot-size SRRL Bale-Opener-Blender for opening and blending cotton have been successfully completed. They indicated that processing through the machine causes no damage to the properties of the cotton fibers. A new feed system which supplies a continuous sandwich bale of cotton to the blender was installed on the pilot machine and measured up to expectations. This feed system has proven to have several advantages over the previously used truck feed system which supplied individual sandwich bales: (1) it enables continuous operation without downtime for loading, (2) it provides increased cotton capacity, resulting in less loadings per shift, and (3) since no bale ends need be processed, it eliminates end-of-the-bale difficulties previously encountered. Design of a full-size blender is underway and progressing satisfactorily. The new feed system is being incorporated into the design. Necessary equipment and supplies for construction of the full-size machine is being procured. (S2 1-252)

2. Improved Methods of Feeding the Cotton Card to Produce Higher Quality Textile Products. Research has continued on the two new approaches and mechanisms for feeding the cotton textile card: (1) the Lap-Drafting Apparatus, and (2) the Precarding Apparatus. A full-size Lap Drafter has been installed on a laboratory carding machine for further development. Individual variable-speed drives have been provided for all units of the Drafter to enable establishment of the best operating conditions. Information previously obtained with the bench-model Drafter will be used as a guide. The experimental model of the Precarding Apparatus also has been installed on a laboratory card so that the thin layer of cotton from the apparatus is fed directly into the card. Since the Precarder is flexible with respect to extent to which cotton is worked, thickness of layer produced and production rate, it will be possible to test a wide range of machine variables and operating conditions as to their effect on feed conditions and the quality of the card web. One observation to date is that the apparent quality of the card web changes very little as the quality of the layer fed to the card is varied over a wide range for the same cotton. Research under a new project will be concerned with the development and evaluation of prototype machines from the Lap Drafter and the Precarder. (S2 1-215)

3. Equipment for Removing Short Fibers from Cotton. Investigations of devices for removal of short fibers from cotton have continued. The previously developed counter-rotating cylinder electrostatic fractionator has been modified to enable increasing production rates while maintaining short

fiber removal. On an eight-inch-wide unit, the short fiber removal was 33 percent at 1/2 pound per hour production. The research has shown that, contrary to research reports of others, electrostatic forces applied to cotton fibers can cause the long fibers and short fibers to act differently, and can serve as the basis of devices for fractionating cotton fibers into long and short length groups. Also, preliminary investigations with a mechanical fractionating device have suggested its possible application to the development of a means of removing short fibers and improving fiber parallelization at the textile card. To achieve the latter objective, promising leads from the research will be applied under a recently initiated project. The initial approach will involve a mechanical system for parallelizing the fibers and continuously combing the output web of the card. The device is currently being designed and constructed, preparatory to installing it on a laboratory card. (S2 1-164 (Rev.), S2 1-273)

4. Aerodynamic Systems for Separating Lint Cotton into Individualized Fibers. The contractor (General Applied Science Laboratories, Inc.) has continued investigations of the application of aerodynamic forces for individualizing cotton fibers. An analysis has been made of the separation of cotton fibers from air by means of a branching canal. By finding the streamlines of the air and the trajectories of the lint particles, the ratio of the percentage of the upstream lint extracted can be found and an efficient geometry determined. An analysis has also been made to determine the forces necessary to extract a cotton fiber from a clump of fibers. A significant achievement was the development of equations relating aerodynamic parameters to the separation of clumps of cotton into individualized fibers. These equations will be a worthwhile tool to aid research and industry in designing better equipment for producing cotton textiles with improved properties. An investigation is also in progress to study the unsteady motion of tangled fibers resulting from sudden decompression in a dilation chamber. Research under this contract has disclosed the fundamental mechanism of forces involved in fiber disentanglement and the complexity of the problem. (S2 1-204(C))

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Improved Mechanical Processing Machinery - Opening Through Carding

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AREA NO. 4 - COTTON - IMPROVEMENT OF WASH-WEAR PROPERTIES

Problem. Garments which are wrinkle resistant and suitable for wash-wear use are increasingly important to the consumer. Although much progress has been made toward securing this market for cotton, much additional information is needed to hold and expand cotton's share of this enormous market. According to recent industry estimates 1.2 million bales of cotton are used annually which would not have been utilized except for the wash-wear development. Projected estimates indicate that in the future most apparel and almost all household textiles will be given a wash-wear or a minimum-care finish. Research on synthetic fabrics is mainly aimed at this lucrative market and is several times greater than the entire utilization effort on cotton. At the same time chemical firms are reducing their research in the development of cotton wash-wear finishes. Promotional advertising claims on cotton wash-wear products have exceeded the actual achievement, and many problems remain to be solved. Much fundamental information is needed to explain mechanisms of the reaction of cotton with crosslinking agents as a basis for the development of new and better wash-wear finishes and for the improvement of present processing techniques. Much applied information is needed which, while essential to the maximum utilization of cotton, is generally beneficial to all processors and therefore comparatively unattractive financially to individual companies. Areas in which research is needed to improve wash-wear cottons include processing techniques, fabric appearance, durability, and comfort. Fabric appearance involves the ability to dry smoothly, resistance to wrinkling or mussing during wear, resistance to dry, wet, and oil soiling, introduction of durable creases as desired, dimensional stability and elimination of seam pucker. Durability involves tensile and tearing strength and abrasion resistance in the finished fabric or garment, as well as resistance to abusive laundring, particularly bleaching and souring. Comfort involves moisture absorption during use, elimination of odor on storage or wearing and, in certain cases, stretchability of fabric.

USDA AND COOPERATIVE PROGRAM

The Department has a continuing long-term program involving organic chemists, physical chemists, analytical chemists, physicists, microscopists, chemical engineers, mathematicians, cotton technologists, textile technologists and textile engineers, engaged in both basic and applied research on wash-wear finishing and improvement of wash-wear properties of cotton. Informal cooperation is maintained with textile finishers, chemical manufacturers, and textile research institutes in connection with the research.

Basic and exploratory research on wash-wear finishing of cotton is conducted at New Orleans, Louisiana. This research is designed to give a better understanding of the chemical reactions and physical changes taking place in wash-wear finishing and the crosslinking of cotton in general. It also

seeks to correlate the properties of the finished cotton with the nature of the crosslinking agent or other treating agent. Basic studies of the relationship of fiber properties to fabric behavior in wash-wear treatments are also conducted. The results provide a broad and sound foundation for the development of new, practical wash-wear finishes for cotton. Additional basic and exploratory research is being carried out under contract at Southern Research Institute, Birmingham, Alabama, on the development of wash-wear cotton fabric with improved moisture absorptivity by use of reactive swelling agents.

Research on the improvement of smooth drying properties--the essential features of a wash-wear fabric--is conducted at New Orleans, Louisiana. Some important phases of current work involve development of new crosslinking treatments and optimum wash-wear fabric structures; investigation of chemical and mechanical treatments to improve strength, resilience, abrasion resistance; and pilot-plant evaluation of promising laboratory finishes. The Cotton Producers Institute cooperates in and supports research to develop optimal cotton fabric structures for men's trousers and dress suits. Additional research on improved smooth drying properties is in progress under contract at North Carolina State of the University of North Carolina at Raleigh, North Carolina, on the effects of mechanical treatments of fabrics prior to, during and following resin finishing on ease-of-care properties.

Research to develop new and improved processing methods for the production of wash-wear cotton yard goods and garments is carried out at New Orleans, Louisiana. Processing methods are being investigated for the production of wash-wear cotton stretch goods with improved durable creases, shape holding properties and abrasion resistance. Cost estimates for new chemicals and for processing of cotton are made to aid industrial establishment of various research developments. Additional processing research is being conducted under contract at Georgia Tech Research Institute, Atlanta, Georgia, to develop improved cotton sewing thread for wash-wear fabric structures, compatible with existing high-speed manufacturing methods, which will not cause seam pucker, or which will have a markedly reduced tendency to cause seam pucker.

Other basic and exploratory research on wash-wear cotton fabrics is in progress under a grant of P. L. 480 funds to the Swedish Institute for Textile Research, Gothenburg, Sweden, for investigation of the mechanism of crease formation and recovery in ease-of-care treated cotton fabrics (project duration -- 4 years.).

The Federal in-house scientific effort devoted to research in this area totals 32.6 professional man-years. Of this number 11.5 is devoted to basic and exploratory research on wash-wear, 19.1 to research on improved smooth drying properties, and 2.0 to new and improved processing methods. The contract research involves an additional 3.0 man-years, 1.0 being on basic and exploratory research on wash-wear, 0.8 on improved smooth

drying properties, and 1.2 on new and improved processing methods. P. L. 480 research involves 1 grant on basic and exploratory research on wash-wear.

PROGRAM OF STATE EXPERIMENT STATIONS

(A general program statement is given under Area 1)

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Basic and Exploratory Research on Wash-Wear

1. Basic Studies of Recovery from Wrinkling and Creasing. Basic investigations of the relation of dry and wet recoveries to wash-wear properties have continued. Determinations of tensile recovery and strength of single cotton fibers for several types of modified cottons (formaldehyde-, dimethylolethyleneurea-, monomethylolethyleneurea-, and oleyl chloride-treated) indicate that fibers are seemingly more sensitive but more variable than low-twist yarns for determining the elastic recovery of wash-wear cottons. Loss in breaking strain is proportionally greater in fibers than in yarns especially for the wet formaldehyde treatments. Recoveries due to the pad-dry-cure of yarns are all of the same type. The immediate recovery values reach a maximum near 65% relative humidity. Per crosslink, dimethylolethyleneurea improves recoveries more than does formaldehyde, but formaldehyde-treated cotton crosslinked to 100% total recovery has a minimum immediate recovery at low strains under standard rather than wet conditions. Oleylated cotton, with its greatest improvement being in delayed recovery, is least sensitive to moisture, and has the largest reduction in modulus. Relationships of strain recovery and energy recovery have been confirmed for several additional types of wash-wear treatments. This indicates that energy recovery, which is more easily and rapidly determined than strain recovery, can be substituted for the latter.

More recent work has placed emphasis on the use of torsional measurements rather than tensile recovery measurements. Torsional properties of cotton fibers chemically treated with formaldehyde and with DMEU were determined for several humidities. The technique devised for this work--wherein the single fiber is the support filament of a torsion pendulum--is more promising than tensile recovery measurements for characterizing differences in recovery properties of fibers at low deformations. It has been found that, upon wetting, the rotational amplitude (self-imposed rotations) of the resin-treated fiber is about one-half that of the untreated (alcohol extracted) fiber. Fibers from which the DMEU has been stripped with acid display essentially the same rotational amplitude as untreated fibers. The rotational frequency (recovery time for imposed turns) is about 145% faster for the resin-treated than for the untreated fibers. Low torsional deformations are completely recoverable in untreated cotton and in those resin-treated cottons investigated thus far. Information being obtained in this research on properties at low deformations, and under conditions of apparent complete tensile recovery as indicated by present tensile tests,

could lead to a better understanding of the mechanism of recovery in chemically treated cotton and those treatments which produce the desired mechanical behaviors. (S2 1-262).

In further research on relationships of fiber properties to fabric behavior in wash-wear treatments, it was found that cellulose density as measured by the gradient column technique is decreased by tension during resin curing of scoured materials but increased by tension on slack mercerized. Density decreases as add-on increases. Fabric structure was found to be relatively unimportant in abrasion resistance of resin treated twill fabrics, but type of resin and scouring or mercerizing prior to resin treatment have pronounced effects on the abrasion resistance at comparable wash-wear rating of fabrics. Fabric structure is important in both abrasion resistance and wash-wear rating of scoured fabric before resin treatment. The research studies have revealed the need for more clearly defined relationships between fiber friction and crease recovery when softeners are added. Friction restrains fiber movement in crease formation and hinders recovery after the crease has formed. It has been found that high concentrations of softeners decrease wrinkle recovery of cotton fabrics, indicating a cementing effect. At low levels of softener, wrinkle recovery may or may not be increased, possibly depending on the wax present in the scoured fabric. Since this unexplained behavior is in an area of research of particular importance to wash-wear treatments both in crease recovery and abrasion resistance, it will be investigated further as one phase of a new project concerned with a study of the relation of fiber properties to physical behaviors of mechanically and chemically treated cotton fabrics. Samples required for the research are being prepared. Cottons of three varieties differing in strength and elongation--Hopi Acala, Pima S-2, and Deltapine 15--have been processed into fabrics of different structures, identical for all three cottons. The fabrics are being scoured and portions of the scoured fabrics will be slack mercerized. Both the scoured and the mercerized fabrics will be resin treated with various tensions applied prior to curing. (S2 1-198, S2 1-272).

The research on effects of time and environmental conditions on the rate of wrinkle recovery of wash-wear cotton textiles has been terminated. The greatest difference in rate of wrinkle recovery is found in the first 2.5 seconds of the standard wrinkle recovery test. There is relatively little change in the shape of recovery curves after about 2.5 seconds of recovery time. However, the final level of wrinkle resistance achieved is greatly influenced by such factors as type of laundering and drying, atmospheric humidity and moisture content of the fabric. Laundering, either by home-type or commercial procedures, decreases the wrinkle resistance of wash-wear cottons but does not affect the shape of the rate of recovery curves. The rates of wet crease recovery of four types of wash-wear cottons were similar to those obtained in the standard test atmosphere (70°F. and 65% RH). Long-time creasing (64 hrs.) lowers the initial, standard, and 20-minute crease recovery angles of crosslinked cottons. However, the rate of recovery appears to be essentially unchanged. Wash-wear cottons creased at

one humidity and relaxed at another were found to exhibit different levels of wrinkle resistance than when creased and relaxed at the same relative humidity. The rates of recovery, however, appear to be essentially the same after the initial opening of the test specimen. Hydroxyethylated cotton, a noncrosslinked cotton which is highly swellable in water, has a relatively high wet crease recovery angle. The shape of its recovery curve after about 2.5 seconds of recovery time is essentially the same as observed for crosslinked cottons. (S2 1-203).

2. Basic Investigations to Improve the Properties of Wash-Wear Cottons. Contract research is in progress at Southern Research Institute to develop wash-wear cotton fabrics with improved moisture absorptivity by use of reactive swelling agents. In initial experiments, cotton printcloth treated with methylolated N,N'-dihydroxyethylenebisacetamide or the corresponding bisurethan was found to have greater moisture absorptivity than samples treated with either dimethylolethyleneurea or dimethylolethyltriazone. The two bisamides will be examined further, and other hydrophilic groups will be applied with crosslinking agents. (S2 1-239(C)).

Research has been initiated to obtain basic information on the properties which are important for resistance to edge abrasion damage in wash-wear cottons, particularly durably creased garments, and to develop methods for improving the resistance of cotton to such abrasion. Initial experiments, in which a number of selected polymers have been applied to cotton fabrics in conjunction with crosslinking agents, have given promising results. It has been found that polymers that improve fabric hand or softness (silicones) generally improve cuff wear life. On the other hand, polymers that are both tough and stiff do not increase resistance to edge abrasion to any extent. Mercerization (either slack or slack followed by restretching) significantly improves wear life (resistance to abrasion) of cotton fabrics treated with almost any wash-wear agent. Lower curing temperatures and use of reactive softeners have also reduced edge abrasion in wash-wear cottons. Special attention will be given to investigation of the use of polymers in combination with mercerization and a wash-wear treatment, and the use of reactive softeners in conjunction with other treatments. (S2 1-260).

B. Improved Smooth Drying Properties

1. Development of Treatments to Improve Strength, Resilience and Other Desirable Properties of Wash-Wear Cottons. The research to produce improved wash-wear cotton through swelling treatments has met with limited success thus far. Although mercerization under conditions which give high swelling retention prior to crosslinking results in increased wet wrinkle recovery of the crosslinked cotton fabric, this approach does not overcome the adverse effects of mercerization itself on wash-wear properties. Use of inert additives, either organic or inorganic, has much less effect on swelling than does the modified mercerization. Phosphoric acid produces a swelling effect equaling or exceeding that from mercerization but produces other adverse side effects. New swelling agents are needed. The importance of

interlamellae regions of the cotton fiber on moisture regain has been confirmed by experiments on viscose. Additives for increasing moisture regain of crosslinked cotton need not be water-soluble or exceptionally high boiling. Studies on specific volume of crosslinked cottons will be made to provide a direct measure of swelling ability. Other work has led to the development of highly active catalysts which will allow the use of crosslinking agents formerly difficult to cure, and the use of milder curing conditions with common agents. The catalysts are made from magnesium chloride and a compound from a wide range of hydroxy or alkoxy substituted carboxylic acids. (S2 1-235).

Investigation of the crosslinking of cotton with new types of N-methylol and related derivatives has continued. An acrylamide-aspartic acid adduct was prepared and found to produce fabrics having intermediate crease recovery angles. Experiments with glycine-acrylamide derivatives showed that 10-12% concentrations were required to produce the best wash-wear fabrics. A phosphonic acid analog of a glycine-acrylamide has been prepared and is being used, after methylolation, in laboratory studies as a crosslinking agent for cotton. It is hoped that this agent will provide flame retardant properties as well as wash-wear properties. Another agent--4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone--looks promising in delayed cure procedures because there is no possibility of formaldehyde release during storage or in use. Hydroxylation of N,N'-ethylenic amides appears to be a new synthesis path for formation of N-methylol type derivatives. It is expected that many such derivatives, which are promising crosslinking agents and are unavailable from normally used synthesis paths, may be obtained in this manner. (S2 1-227).

Research to develop wash-wear finishes for cotton based upon carbamate finishing agents continues to show promise. Dimethylol hydroxyethyl carbamate and dimethylol hydroxypropyl carbamate, two new agents developed in the work, have good potential. Lightfastness of dyed cotton fabrics finished with these agents is markedly better than that of fabrics finished with simple monoalkyl carbamates. With proper finishing conditions the new agents produce durable finishes having good wrinkle and chlorine resistance. Also, the potential cost of the agents is low. They appear to be good agents for deferred cure finishing to produce durably creased, wash-wear cotton garments. Dimethylol hydroxyethyl carbamate is currently being evaluated in wash-wear finishing by several textile finishing companies. Two other new carbamate finishing agents, dimethylol methoxyethyl carbamate and dimethylol benzyl carbamate, have also been prepared in the research and used to produce wrinkle- and chlorine-resistant cotton. Present emphasis in the work is on deferred cure agents. (S2 1-230).

The experimental work in research studies of stretching and compressive shrinkage effects in ease-of-care fabric treatments has been completed by the contractor (North Carolina State of the University of North Carolina at Raleigh). Analyses of the data are in progress. Preliminary results indicate that smooth-drying properties of fabrics are not affected

appreciably by the stretching or compressive shrinkage in processes prior to curing. However, many other properties are affected by the mechanical processes, and it should be possible to utilize those mechanical processes which are advantageous in improving serviceability without affecting smooth-drying qualities of the fabrics. DMEU treatment was not as effective as either APO or DMEC (dimethylol ethyl carbamate) treatment in maintaining smooth drying properties of fabrics subjected to commercial launderings. (S2 1-183(C)).

Recent work has shown that high wrinkle resistance (wet or dry), essentially unchanged abrasion resistance, medium levels of wash-wear performance, lowered stiffness and unchanged tear strength are obtainable in all-cotton fabrics treated with crosslinked silicone films. The cellulose itself is not crosslinked. Dimethyl silicones of molecular weights 12,000-130,000 are cured with benzoyl peroxide on the fabric to give crosslinked films surrounding individual fibers. The efficiency of polymer insolubilization increases with increasing molecular weight. When the silicone treatment was applied to lustrous broadcloth woven of tension-mercerized yarn, the fabric gave a wash-wear rating of 4.0, retained considerable luster, had the same extraordinarily high tear strength as the untreated fabric, and its crease recovery was high (283° dry; 283° wet). After 5 launderings these values did not change, and the flex abrasion resistance of the fabric was 91% of that for laundered, untreated fabric. It has also been found that the silicone and benzoyl peroxide catalyst can be used to replace 50-66% of the cellulose crosslinking agent usually needed to impart a high level of wrinkle resistance. The formulation on slack mercerized cotton fabric gave a fairly high wash-wear rating (4.0), high tearing and breaking strength, and high flex abrasion resistance. Thus it may be possible to prepare wash-wear stretch fabrics of high abrasion resistance by using only enough cellulose crosslinking agent to prevent growth and permanent deformation on repeated flexing, and relying on the silicone and peroxide to impart easy-care properties. Delayed curing systems utilizing silicone finishes will be studied. This approach appears to have potential for avoiding the large losses of abrasion resistance common to delayed cure finishing. (S2 1-253).

2. Development of Optimum Wash-Wear Fabric Structures. Further analysis and summarization of data obtained in the research on relationships between fabric structure and ease-of-care performance of cotton fabrics has been carried out by the contractor (Fabric Research Laboratories). The research has shown that fabric structure effects are greater in heavier than lighter weight fabrics when the fabrics are treated to the recommended resin add-on to insure high wash-wear rating. Fabric structure is extremely important in smooth drying behaviors of scoured and mercerized fabrics. It was found that the more open weave fabrics and fabrics of long floats have distinct advantages in smooth drying and usually have higher tearing strength than the tight and square weave fabrics even after wash-wear treatments. Mercerization improves both smooth drying properties and tearing strength. The smooth drying properties of fabrics after tumble drying were more reliably estimated from crease recovery at 120°F., 15% R. H. than at standard

condition (70°F. 65% R.H.) or at any of several other combinations of moisture and temperature within this range. Temperature and humidity effects on flexural rigidity are very small. The resin treated mercerized fabrics generally decrease in stiffness while the scoured fabrics, especially with the tight weave, increase in stiffness with increase in humidity. Fabric stiffness is less important than crease recovery in achieving smooth drying. (S2 1-170(C)).

Cooperative research with the Cotton Producers Institute to develop optimal cotton fabric structures, for men's trousers and dress suits is in progress. DMEU-crosslinked, experimental fabric structures, formed into trouser cuffs and sleeves and in some instances crosslinked a second time to simulate delayed-cure conditions, were tested for wearability by repeatedly washing and tumble drying. Three popular weave types--twill, plain, and worsted (double cloth construction)--were studied. After 30 wash cycles, the simulated delayed-cure samples showed limited wear, but were superior to the other samples in smooth-drying properties and retention of creases. In the twills, those with a 63° twill angle outperformed those with a 45° twill angle. Based on these preliminary exploratory experiments, fourteen experimental fabric sturctures, including printcloth, gabardine and seer-sucker weaves, were prepared, treated with DMEU resin, and fabricated into trouser cuffs which were pressed and then cured in an oven. The cuffs were tested for wearability via repeated launderings using conventional and modified (extended) laundering procedures. Wear was found to be greatest when the tumble drying time was extended, and least when the washing time was extended. In another experiment, laundering tests (30 launderings) were carried out on similar test cuffs made from fabrics woven from slack mercerized stretched yarns, except that in this case a commercial delayed cure resin was used. Preliminary study of the results indicated that the fabrics woven from the premercerized yarns gave improved wearability.

Two hundred yards of one of the promising experimental fabrics (a gray-striped, summer-weight seersucker woven from similarly premercerized Pima S-2 cotton yarns) have been supplied to the National Cotton Council for commercial finishing, fabrication into suits, and service testing during the summer. The yarn premercerization procedure gives considerable promise of improving wearability of permanent press cotton garments. Test fabrics are currently being woven from commercial tension-mercerized yarns for use in studying the effect of yarn ply twist on fabric wearability. (S2 1-254).

C. New and Improved Processing Methods

1. Wash-Wear Cotton Stretch Goods With Improved Properties. The project to investigate finishing treatments for the production of wash-wear cotton stretch fabrics with improved strength, drape and hand has been terminated. The improved fabric strengths achieved by restretching slack mercerized samples have been further increased by inducing greater swelling by diluting the caustic in the impregnated fibers prior to restretching of the fabrics. Crystalline conversion to cellulose II is not extensive for slack mercerized

fabric and is even less after restretching. Therefore, better realignment of stress-bearing areas within the fibers rather than crystalline changes seems to be the mechanism whereby improved strength is achieved. Recent studies on fabrics having different yarn and fabric structures have shown that loss of breaking strength of fabrics which are slack mercerized, restretched, and then crosslinked may be reduced, depending on type of yarn used. Employing a two-ply yarn gives less strength loss, compared to the grey fabric, than when a singles yarn is used. In some cases essentially 100% of the breaking and tearing strengths of the grey fabric have been retained. Work along these lines is being continued under other projects directed toward producing wash-wear fabrics and garments with improved abrasion resistance. (S2 1-211).

Exploratory experiments have indicated that preferential crosslinking of cotton in selected regions of the fabric structure is a promising new approach for improving abrasion resistance of durably pressed, wash-wear cotton garments. Two techniques have been developed for crosslinking the back side of a fabric, leaving the front (wearing) side uncrosslinked for improved abrasion resistance: (1) direct back coating with a viscous solution of a crosslinking agent, and (2) use of a catalyst-inactivating reagent for face coating a fabric previously impregnated with a crosslinking agent but not cured. These procedures should lead to reduced processing costs since less crosslinking agent would be required. Also, resins which tend to cause yellowing of white goods could be employed since the discoloration would be on the back side only. Use of preferential crosslinking on slack mercerized, partially restretched fabrics shows particular promise for improving wear life. However, evaluation tests of trouser cuffs by home washing and tumble drying showed some wear on all samples, indicating that additional research will be needed to develop a satisfactory durable press treatment for 100% cotton garments. Polymer additions and surface reactions will be investigated to reduce fibrillation and dye fading at creases and seams of durably pressed garments.

2. Development of Improved Cotton Sewing Thread for Wash-Wear Cotton Products. Research is being conducted under contract at Georgia Tech Research Institute to develop improved cotton sewing thread for wash-wear fabric structures, compatible with existing high-speed manufacturing methods, which will not cause seam pucker or which will have a markedly reduced tendency to cause seam pucker. The contractor has obtained all fabrics and threads required for the research. Physical characteristics of these materials have been determined, and sewing tests have been initiated to evaluate the physics of seam pucker. Initial sewing tests will be on printcloth samples, to be followed later by the other types (oxford, broadcloth, and gingham). A photoelectric procedure for objectively measuring seam pucker shows promise and its development will be continued. (S2 1-228(C)).

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AREA NO. 5 - COTTON PRODUCTS WITH SPECIAL PROPERTIES

Problem. In many uses where special properties are of paramount importance, cotton is being replaced by synthetic materials. To improve its position in the textile market, which has declined from 79.5% of mill consumption of all textile fibers in 1939 to an estimated 55% in 1964, new applications must be explored and improved products developed to meet the competition of synthetic fibers. Cottons having high recoverable stretch, durable loft, light-weight bulk, pleasing textures, warmth and other highly desirable properties are needed to enable cotton to compete successfully with synthetic fibers in the rapidly expanding market for stretch and bulked type fabrics. Fabrics designed to achieve increased resistance to tearing and abrasion, flex life and other strength properties are needed to improve the wear life of cotton textiles for apparel, household and industrial uses. Cotton fabrics must be designed to withstand better the elements of weather and finishes developed that will provide greater protection from solar radiation, microorganisms, acids and fire, and that will resist color change. Additional basic information must be developed to improve cotton's resistance to water and oil-borne soils, and to dry soiling. Resistance to soiling ranks fifth in importance among the 40 end-use qualities for textiles. Cheaper and more durable flame retardant finishes for cotton, specially for outdoor use, are needed. Numerous consumer preference surveys have shown that a great potential demand exists for cotton material that will be more lustrous without sacrifice of functional properties. Cotton textiles with multipurpose finishes are also needed, particularly those where several desirable end-use properties can be introduced in a single process. Improved insect-resistant cotton bags for the storage and shipment of food commodities is another type of cotton product that must be developed.

USDA AND COOPERATIVE PROGRAM

The Department has a continuing long-term program involving organic chemists, analytical chemists, physical chemists, physicists, microscopists, chemical engineers, cotton technologists, textile technologists, and textile engineers engaged in both basic and applied research to develop new or improved cotton products possessing special properties to meet the competition of synthetic fibers and other synthetic materials in various end uses. Informal cooperation is maintained with textile finishers, chemical manufacturers, and textile research institutes in connection with the research.

Research is carried out at New Orleans, Louisiana, in cooperation with the Foundation for Cotton Research and Education (affiliated with the National Cotton Council of America) and the Canvas Products Association International, to develop cotton fabrics with improved resistance to outdoor weathering. This research includes discovery of new and more effective biocides, and

sunlight-resistant pigments for cotton textiles; and development of improved formulations, equipment and procedures for producing weather resistant cotton textiles including those having durable color and water repellency in addition to weather resistance. Additional research is being conducted under contract at Texas Woman's University, Denton, Texas, on development of weather-resistant, water repellent finishes for cotton; and at Southern Research Institute, Birmingham, Alabama, on investigation of interfacial and graft polymerization procedures for producing weather-resistant cotton textiles with improved physical properties.

Research to develop new fluorochemical finishes for oil- and water-repellency and other reactive and additive finishes is conducted at New Orleans, Louisiana, to improve cotton's soil resistance. Additional research is being performed: (1) under contract at the Harris Research Laboratories, Inc., Washington, D. C., to provide fundamental information on the mechanism of the soiling of cotton by dry soils, and water-, oil- and solvent-borne soils, which could lead to the formulation of a general theory of the soiling of cotton and modified cotton; and (2) under a grant at the University of Arizona, Tucson, Arizona, on correlation of surface microtopography of treated and untreated cotton fibers with resistance to soiling of cotton textiles.

Research on flame-resistant cotton textiles is peformed at New Orleans, Louisiana. Emphasis is on the development of durable inexpensive flame retardants for cotton, and treatments to impart flame resistance to cotton while at the same time imparting other desired textile properties.

Investigations of methods for imparting durable luster and related appearance characteristics to cotton textiles are carried out at New Orleans, Louisiana. Current research is concerned with the development of lustrous wash-wear fabrics with increased strength and durability.

Research to improve cotton's bulk, elasticity and resilience through resin treatment, chemical modification, slack mercerization and other type swelling treatments, of fibers, yarns and fabrics is conducted at New Orleans, Louisiana. The research on fibers is aimed primarily at the development, by chemical or mechanical means or both, of more resilient and cohesive cotton batts for use in mattresses and other padding applications in the furniture and automobile industries. The cotton batting research is conducted cooperatively with the National Cotton Batting Institute, Textile Waste Association, National Cottonseed Products Association and the Foundation for Cotton Research and Education (affiliated with the National Cotton Council of America). Work on yarns is intended to produce bulky, elastic yarns suitable for weaving or knitting into fabrics with improved stretch and bulk characteristics. Investigation of a slack mercerization process with and without subsequent resin treatment, is being carried out to achieve improved stretch cotton fabrics for industrial, household and apparel uses. The influence of yarn and fabric structures on the properties of the stretch fabrics is being studied. Additional research on stretch and bulked cotton

products is being carried out under contracts at North Carolina at the University of North Carolina at Raleigh, Raleigh, North Carolina, on evaluation of stretch-type cotton yarns (prepared by backtwisting and false-twisting techniques) in knit wear; and on determination of optimum yarn constructions, knitting structures and prefabrication design for producing stretchable articles of knitted cotton wearing apparel by slack mercerization; and at Clemson Agricultural College, Clemson, South Carolina, on development of cotton knit fabrics having increased bulk, warmth, and dimensional stability by application of finishing agents.

Research to develop improved insect-resistant cotton bags for the storage and shipment of food commodities was recently initiated at New Orleans, Louisiana. The Stored-Product Insects Research and Development Laboratory, Market Quality Research Division, ARS; bag manufacturers; and the Textile Bag Manufacturers Association cooperate in the work.

The Federal in-house scientific effort devoted to research in this area totals 25.9 professional man-years. Of this total, 6.0 is devoted to weather resistant cotton fabrics, 2.3 to soil resistant cotton textiles, 6.8 to flame resistant cotton textiles, 2.0 to cotton textiles with improved luster, 5.5 to stretch and bulked cotton products, and 3.3 to insect-resistant cotton bags. The domestic contract and grant research involves an additional 6.9 man-years, 1.5 being on weather resistant cotton fabrics, 2.3 on soil resistant cotton textiles, and 3.1 on stretch and bulked cotton products.

PROGRAM OF STATE EXPERIMENT STATIONS

(A general program statement is given under Area 1)

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Weather Resistant Cotton Fabrics

1. Improved Biocides, and Sunlight-Resistant Pigments for Cotton Textiles; and Improved Formulations, Equipment, and Procedures for Producing Outdoor Cotton Textiles. In cooperative research on weather resistant cotton fabrics with the Canvas Products Association International and the Foundation for Cotton Research and Education, studies of zirconyl acetate - and zirconyl ammonium carbonate - metal salt fungicides have continued. Cotton duck treated with one of these agents--copper zirconyl boroacetate--has completely resisted mildew and algae growth for more than 36 months of outdoor exposure. Five companies are currently using these new treatments for commercial production of outdoor weatherable cotton fabrics. Recent work has shown that copper salts solubilized with zirconyl acetate or zirconium ammonium carbonate can be effectively cured on cotton fabrics at 80°C, whereas optimum curing temperatures for phenylmercury derivatives vary between 80°C and 130°C depending on the particular derivative employed. Of particular practical importance is the fact that the phenylmercury

derivatives of zirconium which have been deposited on fabrics have much greater resistance to water leaching than the amine-phenylmercury agents now in use. Several new phenylmercury compounds have been prepared by a new method of synthesis, and found to have very good rot resistance as determined by soil burial tests. Combinations of several metals with zirconium have been found to give additive fungicidal effects but little evidence of synergism to date. Other metallic ion combinations are being investigated in attempts to discover synergistic combinations. (S2 1-259).

Other cooperative work is concerned with the development of multipurpose finishes for outdoor cotton fabrics. Cotton fabric samples treated with clear base finishes based on methylolmelamine and coated with pigmented vinyl resins have withstood one year of outdoor exposure without loss of strength. This performance should be of considerable interest to finishers of outdoor fabrics. It has been found that if methylated methylolmelamine is substituted for methylolmelamine, a considerable increase in useful storage life of the resin-zirconium acetate treating solution is obtained. Fabrics finished with methylated methylolmelamine are currently being evaluated for weather and rot resistance. A method has been devised for determining the reflection, absorption and transmission characteristics of treated and untreated outdoor cotton fabrics. The measurement of the sunlight ultraviolet optical characteristics of these fabrics, when compared with the fabrics' outdoor performance, may possibly afford some insight into the mechanisms of actinic degradation and/or protection. Studies of the role of atmospheric contamination in cotton fabric degradation at various continental United States sites are also in progress, in cooperation with the Air Pollution Division of the U. S. Department of Health, Education, and Welfare. (S2 1-256).

Based on completed initial phases of the contract research at Texas Woman's University to develop weather-resistant, water-repellent finishes for cotton, the best water repellents have been selected and are being tested in combination with four selected weather-resistant finishes. When exposure tests of the fabrics at various environmental sites are completed, much useful information concerning these types of finishes will become available. (S2 1-200(C)(Rev.)).

Contract research has been initiated at Southern Research Institute to investigate interfacial and graft polymerization procedures for producing weater-resistant cotton textiles with improved physical properties. The factors controlling the amount and uniformity of graft polymerization of acrylonitrile onto cotton printcloth have been studied in some detail and the evaluation of the grafted products has been started. The most uniformly grafted products were obtained by radiation initiation or by ferrous ion-initiation with the solution method of monomer application. The ceric ion-initiation method gave more rapid reactions than other methods investigated. A polymer add-on greater than 10% stiffened the fabric appreciably and, in some cases, the fabric structure was noticeably tightened by the treatment. Microscopic examination showed definite differences in the products obtained by the different grafting methods. This method of

finishing cotton has potential for imparting many new properties. (S2 1-245(C)).

B. Soil Resistant Cotton Textiles

1. Basic Studies of Soiling and Soil Removal. The contractor (Harris Research Laboratories, Inc.) has obtained additional fundamental information on the dry soiling and oily soiling properties of cotton fabrics, some of which were crosslinked with formaldehyde at two degrees of swelling, chemically modified to introduce cationic or anionic groups, and/or coated with various finishes having a range of hardness, thermoplasticity, charge, and hydrophobicity. The nature of the coating on the fabric was found to have the greatest effect on dry soiling and laundering. Hardness of the coating was found to influence soiling and soil removal even when the coating was applied to chemically modified fabrics. Generally, crosslinking with formaldehyde results in fabrics which retain more soil in laundering than the noncrosslinked cottons. Form D fabrics (crosslinked in the nonswollen state), especially when subsequently chemically modified, soil less with dry or oily soil and retain more soil during laundering than comparable Form W fabrics (crosslinked in the swollen state). Fabrics coated with acrylates, regardless of hardness, had only about half the soil removed when drycleaned. Soil redeposition in dry cleaning was especially heavy among finishes from which soil was difficult to remove. The basic findings will be useful in developing new soil resistant finishes for cotton. (S2 1-223(C)).

Research was recently initiated under a grant at the University of Arizona to determine the surface microstructure of untreated and of chemically finished cottons with relation to soil attraction and soil retention. A high-resolution electron microscope has been installed by the grantee for use in the research. Techniques for making replicas of the surface of cotton fibers are being perfected, preliminary to initiating studies of soiling. The research should lead to a better understanding of the soiling of cotton and point the way to improvements in soil resistance. (S2 1-238(Gr.)).

2. Development of Fluorochemical and Other Soil Resistant Finishes for Cotton. Research to develop durable water- and oil-repellent finishes for cotton fabrics through the use of fluorochemicals has continued. The 1,1-dihydroperfluoroamines, for which a high-yield method of synthesis was recently devised, have been shown to be useful in incorporating long-chain perfluoroalkyl groups onto cotton cellulose. These amines are not cellulose-reactive but can be attached via reaction with cellulose-reactive materials such as THPC, THPC-urea precondensates, and modified polyethylenes. The perfluoroalkyl groups render the fabric oil repellent and, depending on the material used to attach the fluorochemical to cotton, water repellency may also be improved. Experiments are in progress to attempt to increase water repellency and lower strength losses from these treatments. Due to the extreme instability of alpha-chloromethyl fluoro ethers, further research on the modification of cotton with these agents has been abandoned. (S2 1-250).

C. Flame Resistant Cotton Textiles

1. Treatments to Impart Flame Resistance and Improved Textile Properties to Cotton. To increase the acceptance of flameproofing finishes by industry, research is in progress to develop durable inexpensive finishes. Inexpensive organic and inorganic compounds were added to APO, APO-THPC, and THPC-urea flameproofing agents with a significant reduction of the amount of expensive phosphorus compound needed. Although some of these modified finishes rendered cotton fabrics flame resistant, some of the fabric properties, such as durability and strength, were not as good as desired. Nevertheless, this approach warrants further investigation. In other work, it was found that the efficiency of the previously developed THPC-urea-NH_3 flameproofing process is increased by raising the pH level of the precondensate with sodium hydroxide. Cotton stretch fabrics were made flame resistant by application of this and other standard finishes, at the same time improving recovery properties of the fabrics. Flame retardancy has also been imparted to cotton fabrics by application of formulations consisting of bromendic anhydride, urea, and THPC. THPC has also been reacted with selected nitrogen-containing compounds and with polyhydroxy compounds to form highly crosslinked flame-resistant polymers. Evaluations of these materials are continuing, with emphasis on developing nonyellowing, strength-retaining finishes.

Use has been made of differential thermal analyses (DTA) and thermogravimetric analyses (TGA) for studying the mechanism of flame resistance. DTA thermograms indicated differences in decomposition characteristics between phosphorus type flame-resistant finishes and halogen type finishes. All of the flame-resistant fabrics decomposed at considerably lower temperatures than untreated cotton. TGA thermograms of flame-resistant samples showed more rapid weight losses and larger residues than those of untreated cotton. When the fabrics were heated under oxygen rather than nitrogen, decomposition was more complete and residues were smaller. Utilization of basic findings from this work should be helpful in the development of improved flame-retardant finishes for cotton. (S2 1-257).

Investigations to impart multifunctional properties--including flame resistance, crease resistance, rot resistance, improved dyeability, etc.--to cotton in a single treatment are continuing. Two new organophosphorus compounds with cellulose reactive chlorohydrin groups were synthesized: bis(1-hydroxy 2-chloroisopropyl)phosphinic acid, and bis(1-hydroxy 2,2'-dichloroisopropyl)phosphinic acid. Also, a simple method of preparing bis(chloromethyl) phosphinic acid in good yield was discovered. These three compounds were found to crosslink cotton in the presence of sodium hydroxide to produce fabrics with good wet wrinkle recovery, increased moisture regain, ion-exchange properties, increased receptivity to basic dyes, and a degree of flame resistance. In another phase of work, it has been discovered that the strength of cotton fabric treated with the formic acid colloid of methylolmelamine can be significantly increased by partial acid hydrolysis of the finish, at the same time maintaining considerable rot resistance. Research will be carried out on the preparation of aminomethyl phosphinic

acids (and esters) from chloromethyl phosphinic acids and ammonia. These compounds will be used as intermediates in the production of polymers on cotton to impart multifunctional properties. (S2 1-251).

D. Cotton Textiles With Improved Luster

1. Processes for Imparting Durable Luster and Increased Strength and Durability to Wash-Wear Cotton Textiles. Research is in progress to develop lustrous wash-wear fabrics with increased strength and durability. Various methods of yarn mercerization were investigated. Two-ply yarns of several varieties of cotton, both rain-grown and irrigated, mercerized at normal length (NL), to 3% above NL, or slack and restretched showed no loss in breaking strength after crosslinking with DMEU, when compared to the uncrosslinked grey controls. Most of the yarns mercerized slack and restretched to NL or to 3% above NL showed a gain in breaking strength of 27-45% after crosslinking. The loss in breaking strength of these crosslinked mercerized yarns ranged mostly from 0-10% when compared to the uncrosslinked mercerized controls. By these methods, it would be possible to obtain a wash-wear fabric with considerable elongation as well as high strength retention. A wash-wear fabric with luster and high strength retention could also be made if mercerization is carried out using considerable tension. In the next phase of the research, 60/2 combed grey yarn will be mercerized by different methods, and woven into broadcloth fabrics for crosslinking. (S2 1-267).

E. Stretch and Bulked Cotton Products

1. New and Improved Processes for Production of Stretchable Cotton Yarns and Fabrics Using Chemical and Mechanical Treatments. Experiments to determine the effect of fabric structure and aftertreatments on the properties of both filling-stretch and two-way stretch cotton fabrics woven from stretch yarns produced by crimping resin-treated yarns using the back-twist method have been successfully completed. Fabrics with up to about 90% stretch were produced. It was found that fabric stretch could be adequately controlled by adjusting the thread count, and was also dependent upon the type of weave. Sateen and other weaves with long floats produced fabrics with the most stretch. In general, abrasion resistance improved as the amount of stretch was increased. The dimensional stability, wrinkle resistance, and recovery properties of the stretch fabrics were significantly improved by aftertreatment with a resin to a level of add-on of 3 to 4%. Strengths of the fabrics decreased 5 to 30%, compared to the untreated stretch fabrics. The flat abrasion resistance of the aftertreated fabrics was slightly less than that of the untreated stretch fabrics, but equal to that of untreated, nonstretch fabrics of comparable structures. Fabrics woven from the stretch-type cotton yarns were also aftertreated using a deferred curing procedure to impart permanent creases. Trouser cuffs made from these fabrics exhibited excellent wrinkle resistance, crease retention and wearing qualities after 30 home launderings. The stretch yarns and fabrics developed under this terminated project have created considerable interest in the textile industry and commercialization is anticipated. One textile machinery

manufacturer is in the process of developing high speed falsetwisting equipment for producing cotton stretch yarns commercially. (S2 1-193(Rev.)).

Fabrics with a high degree of easy filling stretch have also been woven from cotton stretch yarns prepared by other combinations of chemical and mechanical treatments, such as acetylation, cyanoethylation, grafting with acrylonitrile, and mercerization, followed in each case by backtwisting. Falsetwisting techniques also proved applicable in conjunction with acetylation or cyanoethylation. The recovery of the various fabrics from stretching was very good; however, due to the large amount of stretch obtained, the percent growth was higher than desired. High and normal twist cotton yarns mercerized under tension and slack, at room and elevated temperatures and in the presence of sodium thiocyanate, and subsequently backtwisted, showed some stretch properties which were carried over into fabric woven from these yarns. (S2 1-213).

In research to develop cotton knit fabrics having increased bulk, warmth, and dimensional stability by application of finishing agents, the contractor (Clemson Agricultural College) has found that improved bulk is dependent not only on technique of application of an agent but also on the type agent used. Vacuum-centrifuge application of tris(1-aziridinyl)phosphine oxide (APO) and dimethylol ethyleneurea (DMEU) has given best overall appearance and dimensional stability of cotton wash-wear knit goods having increased bulk. Results of laundering tests suggest that dimensional stability is being achieved with little change in volume of the fabric. Greater bulking of the fabric is still needed to achieve significantly increased warmth properties to make the process attractive commercially. Improved bulking treatments will be sought through use of tumble drying and curing apparatus, and swelling treatments before and during crosslinking. (S2 1-205(C)).

The contractor (North Carolina State of the University of North Carolina at Raleigh) has now established satisfactory knitting techniques and fabric structures for the production of knit fabrics from 24/2 and 60/2 stretch-type cotton yarns made by the false-twist method, as was previously done for the back-twist method. All of the crew socks and T-shirts required for service testing have been knitted from the stretch yarns produced by the two methods. Preliminary service tests on the garments are now in progress to guide the design of the large service tests scheduled for initiation in September 1965. Information being developed in the research should furnish the industry a sound basis for designing, producing and promoting such stretch fabrics and garments. (S2 1-197(C)(Rev.)).

2. New and Improved Processes for Production of Stretchable Cotton Textiles Using Slack Mercerization and Other Type Swelling Treatments. Further research has been conducted to develop cotton fabrics with improved warp and filling stretch properties by slack mercerization. Experiments on variations in yarn structure of plain and twill weave fabrics have shown that slack mercerization for 1-way stretch produces fabrics with similar stretch properties when low-twist filling yarns are used, regardless of yarn size.

When high-twist filling yarns are used, smaller filling yarns produce fabrics with a greater amount of easy stretch and consequently more growth than those made with larger filling yarns. Both 1-way and 2-way stretch fabrics woven with high-twist filling yarns had more filling stretch and greater growth than those woven from low-twist filling yarns. One-way stretch fabrics had greater easy filling stretch and better recovery than 2-way stretch fabrics. The relative size of the warp and filling yarns had an important influence on the stretch properties of 2-way stretch fabrics, more easy stretch usually being produced in the direction in which the smaller yarns were running. One-way stretch plain weave fabrics had significantly improved warp strength properties after resin treatment if mercerized under warp tension. Fabrics with two-ply warp yarns gained as much as 25% in warp breaking strength and those with singles warp yarns lost less than 20% in warp breaking strength in comparison with their untreated control fabrics. Filling breaking strength losses of stretch fabrics made from either plied or singles yarns were about the same as compared with their controls. The recovery of stretch fabrics woven from plied yarns was greater than that of stretch fabrics woven from singles yarns. Flex endurance in both warp and filling directions was increased by increasing the number of warp ends per inch which also reduced filling growth after cyclic loading tests.

Pretreatment of filling yarns by either scouring, slack mercerizing, or mercerizing at normal length did not give any improvement in the properties of the slack mercerized, finished fabrics. The combination of base-catalyzed crosslinking and slack mercerization resulted in all-cotton stretch yarns with improved wet recovery after stretching; and fabrics woven from the yarns had improved wet recovery after stretching, and better wet wrinkle recovery. (S21-213, S2 1-226).

Contract research on the production of stretchable knitted cotton wearing apparel by slack mercerization is in progress at North Carolina State of the University of North Carolina at Raleigh. Experiments in which shrinkages of yarn in slack mercerized skeins and shrinkages of yarn in knittings were compared have indicated that knitting structures offer restraint to yarn shrinkages even in very loose fabrics. Evidence of correlation between shrinkage of yarn and of loosely-knitted fabric has been obtained. Studies on the skewness of loosely knitted fabrics showed that fabric length was proportional to the angle of skewness which increases with the twist in the yarn being knitted. Preliminary study of slack mercerized yarns showed that: yarn shrinkage was proportional to yarn twist and was not influenced much by yarn count; 10% caustic solution was not sufficient for mercerization when other conditions were normal; yarn shrinkage was reduced at higher caustic temperatures but was not influenced appreciably by wash-water temperatures when 20% caustic was used for mercerization. Loosely-knitted socks will be made, slack mercerized, and evaluated. (S2 1-224(C)).

At least 30 companies are now producing all-cotton stretch fabrics by the slack mercerization process. All-cotton stretch men's hose are also being produced commercially, both by slack mercerizing loosely knit hose and by knitting hose from slack mercerized stretch yarns. This rapid advance in

commercialization of stretch cottons has been achieved to a large degree because of active coordinated research between the Southern Division and commercial weavers, finishers and knitters. Active cooperation is continuing with several companies who are doing development work on stretch fabrics, stretch laces, stretch socks, and the molding of stretch fabrics.

3. Resilient and Cohesive Cotton Batts from Low Cost Cotton. Investigations to improve the production and the performance characteristics of chemically treated cotton batting have continued in cooperation with the National Cotton Batting Institute, the Textile Waste Association, the National Cottonseed Products Association, and the Foundation for Cotton Research and Education. More definitive information on the drying mechanism was obtained through the establishment of the effects of relative humidity, temperature, time, air velocity, static pressure, and pressure differential through the in-process product. Many new resins and latexes, some especially compounded by the chemical companies for application to cotton batting, were evaluated for efficacy in improving the performance of the product. Alternative methods of chemical treatment, including treatment of rawstock, were explored. Also, fiber randomization within the array was further evaluated. Present emphasis in the research is on commercialization aspects. Two major automobile manufacturers have approved the new chemically treated batting--"Cotton Flote"--for use in some of their 1965 models; and one producer of batting has already manufactured and supplied large quantities of Cotton Flote for this purpose. It is anticipated that another major auto manufacturer will approve the product soon. At least seven other batting producers are piloting the process for making Cotton Flote. As the availability of the new product increases, its use will undoubtedly be extended to the bedding and furniture manufacturing industries. (S2 1-181(Rev.), S2 1-269).

F. Insect-Resistant Cotton Bags

1. Development of Improved Insect-Resistant Cotton Bags. Research to develop improved insect-resistant cotton bags for the storage and shipment of food commodities was recently initiated in cooperation with the Stored-Product Insects Research and Development Laboratory at Savannah, Georgia, bag manufacturers, and the Textile Bag Manufacturers Association. Initial work has shown that inexpensive coatings based on wax, or starch (with talc as a filler), can be used effectively to seal commodity bag fabrics. Also, calendering of insecticide-treated fabrics appears extremely promising for this purpose. A number of fabric samples, with and without varying levels of insect repellent treatment, are currently undergoing evaluation at the Savannah laboratory. (S2 1-271).

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AREA NO. 6 - COTTONSEED PROCESSING AND PRODUCTS

Problem. Cottonseed products, currently approximately two billion pounds of oil and 2.8 million tons of meal derived from the annual domestic production of cottonseed, face increasing competition for markets. For its chief market, edible products, cottonseed oil must compete with other vegetable oils and animal fats. The nation's capacity for producing these oils and fats is so great that supplies can be expected to exceed both domestic and foreign demand for some time to come. Improvements in the quality and utility of cottonseed oil are needed to retain present and open new markets for the currently large and possibly greater future production. Cottonseed meal, used chiefly as a protein supplement in feeding ruminant animals, faces serious competition from synthetic urea and other supplements. The quality and nutritive value of the meal must be improved and new outlets developed.

Much research is urgently needed on the fungi and toxic fungal metalbolites which may develop in cottonseed and its processed products. The mycotoxin problem is a potentially serious one for many agricultural commodities. Also, additional information is urgently needed on the chemical, physical, and biochemical properties of cyclopropene fatty acids in cottonseed and means of converting them, if found necessary, into physiologically inert forms. Usually there is discrimination in the markets against 25% to 50% of the production of cottonseed oil due to the presence of reddish colors that are not removed by conventional commercial refining, bleaching and deodorizing methods. It is essential that information be developed on the chemistry of the pigments responsible for the off-colors, and that more efficient means be developed to eliminate them and thus upgrade the oils, particularly for use in margarine and shortening. New types of modified fats, such as polyester and polymeric fats, need to be developed from cottonseed oil for applications in the fields of edible and inedible coatings, waxes, resins, plasticizers, and lubricants. Improved cocoa butter-like fats and other confectionery fats derived from cottonseed oil could also provide new markets for large quantities of oil. Fundamental information is needed on hydrogenation to permit production of improved modified fats and oils. Other areas in which markets for cottonseed oil need to be developed through research include fat emulsions for intravenous feeding, edible emulsifiers, and fatty acid amides and other derivatives for use in various industrial products. Improvement in the quality and nutritive value of cottonseed meal is needed so that it can better compete with other protein feed supplements. Additional information is needed on the physiologically active constituents of the meal responsible for egg abnormalities, swine mortalities and growth abnormalities of young animals that limit cottonseed meal's usefulness in poultry and swine rations, and for the reported implication of cottonseed meal in the incidence of trout hepatoma which has resulted in its elimination from use in fish feeds in certain areas. Processing methods must be devised for the commercial

production of meals that can be fed to broilers, laying hens and swine, safely and without restriction. Procedures for the preparation of cottonseed flours and their derived products for human consumption in developing countries also must be developed. In order to lay the necessary groundwork for further advances in cottonseed research on food, feed and industrial products and processing technology, additional fundamental information is also needed on the chemical composition and properties of cottonseed and of various cottonseed products.

USDA AND COOPERATIVE PROGRAM

The Department has a continuing long-term program involving organic chemists, physical chemists, analytical chemists, biochemists, chemical engineers, physicists, and microbiologists engaged in both basic and applied studies on cottonseed and its products to develop new or extended uses for these materials.

Research to develop fundamental information on the chemical composition and properties of cottonseed products is conducted at New Orleans, Louisiana, as a basis for efficient applied research in the fields of food, feed, and industrial products from cottonseed. Some important phases of current work involve research on the chemical, physical, and biochemical properties of cyclopropene fatty acids and other cottonseed constituents; and on fungi and toxic fungal metabolities which may develop in cottonseed and its processed products. The Foundation for Cotton Research and Education contributes towards research on the isolation and characterization of cyclopropene ring fatty acids of cottonseed. The National Cottonseed Products Association supports a Postdoctoral Research Associateship for conducting pioneering research on cottonseed proteins and biochemistry as a part of the Seed Protein Pioneering Research Laboratory's research. Additional research on chemical composition and physical properties is carried out: (1) under contract at the University of Tennessee, Knoxville, Tennessee, on investigations of gossypol esters and mild oxidation products of gossypol and gossypol derivatives; and at Purdue Research Foundation, Lafayette, Indiana, on fundamental investigations of chemical transformations of olefinic compounds of fats and other agricultural materials by hydroboration and subsequent reactions to develop basic information for the production of useful products; and (2) under a grant at Boston University, Boston, Massachusetts, on the development of procedures for synthesizing C^{14}-labeled malvalic acid esters.

New and improved food products and processing technology are developed in research conducted at New Orleans, Louisiana. In oil research, methods are being sought to produce improved cottonseed oils, and confectionery fats, polyester products, and fat emulsions for intravenous nutrition from cottonseed oil. The research on confectionery fats is cooperative with the National Confectioners' Association who maintain a Fellowship at the Southern Regional Research Laboratory, New Orleans, Louisiana, in partial support of the work, and evaluate promising research products. The Office

of the Surgeon General supports the research on fat emulsions. This research is conducted cooperatively with the U. S. Army Medical Research and Nutrition Laboratory and several medical school research groups. Other current work -- supported by the Agency for International Development -- involves a study of the preparation of cottonseed flours and their derived products for human consumption in developing countries. UNICEF cooperates by arranging nutritional evaluations of experimental products in developing countries, and the Human Nutrition Research Division, ARS, also cooperates by evaluating certain of the products. Informal cooperation is also maintained with industry in connection with the research on new and improved food products and processing technology. Additional research on new and improved food products and processing technology is conducted under contract at the University of Illinois, Urbana, Illinois, on chemical investigations of cyclopropenoids to develop practical means of eliminating or physiologically inactivating the cyclopropenoid constituents of cottonseed oil.

Research is carried out at New Orleans, Louisiana, to develop new and improved feed products and processing technology for cottonseed. Investigations are in progress to isolate and identify the physiologically active constituents in cottonseed meals that adversely affect the utilization of the meal as a protein supplement in nonruminant feeding; to isolate and chemically characterize the constituents of the protein systems of cottonseed to provide a basis for the further improvement of nutrititive value of cottonseed meal; and to determine processing conditions for the production of cottonseed meals of maximum quality -- meals more suitable for feeding to nonruminants such as swine and poultry, as well as to ruminant animals. An important, recently initiated line of work is concerned with the development of economically feasible methods for the inactivation or removal of aflatoxins from contaminated cottonseed and cottonseed products to permit their utilization in feeds (and foods). Animal tests in connection with the overall research program are conducted through the cooperation of nutritionists in State Agricultural Experiment Stations at universities, in the Animal Husbandry Research Division, and in industry. The Pharmacology Laboratory at the Western Regional Research Laboratory, Albany, California, cooperates by conducting animal studies to determine the physiological and pharmacological effects of cyclopropene acids and toxic fungal metabolites. Cooperation is also maintained with the Crops Research Division, ARS, Market Quality Research Division, ARS, the Food and Drug Administration, the National Cottonseed Products Association, UNICEF, and members of the cottonseed industry. Additional research in the field of new and improved feed products and processing technology is in progress under contract at IIT Research Institute, Chicago, Illinois, on development of practical processing methods for inactivation of cyclopropene groups in cottonseed meal that decrease its value as a feed for laying hens.

Research to develop new and improved industrial products and processing technology is conducted at New Orleans, Louisiana. Present emphasis is on amide derivatives of long-chain fatty acids. Informal cooperation is maintained with industrial firms for the evaluation of promising research

products for specific end uses. Additional research on new and improved industrial products is being carried out under contract at the University of Arizona, Tucson, Arizona, on the polymerization of reactive chemical intermediates derived from cottonseed oil and other agricultural materials to produce polymers having potential industrial utility; and at U. S. Industrial Chemicals Co., Tuscola, Illinois, on copolymerization of ethylene with unsaturated fatty acids and other selected derivatives of agricultural materials to extend their utilization in commercial plastics.

Other research on chemical composition and physical properties is in progress under grants of P.L. 480 funds to the following foreign institutions: British Food Manufacturing Industries Research Association, Leatherhead, Surrey, England, for fundamental studies of the fatty acid and glyceride composition of cottonseed oil and the crystallizing behavior of some of the major components (project duration - 4 years); University of Bombay, Bombay, India, for a study of the relationship of substituent fatty acid groups on the physical properties of diacid triglycerides of palmitic and stearic acids as a means of increasing the utilization of cottonseed oil for food and industrial purposes (project duration - 5 years); Israel Institute of Technology, Haifa, Israel, for investigation of π-complexed organometallic compounds derived from polyunsaturated fatty acids to obtain fundamental information needed in expanding the utilization of cottonseed oil (project duration - 5 years); University of Rome, Rome, Italy, for basic investigations on the physical and physicochemical properties of cottonseed proteins (project duration - 5 years); and Commonwealth Scientific and Industrial Research Organization, Ryde, Australia, for an investigation of the chemistry and biological effects of cyclopropenoid compounds that occur in cottonseed and its products (project duration - 5 years).

Additional research in the field of new and improved feed products and processing technology is in progress under grants of P.L. 480 funds to the following foreign institutions: Instituto Farmacologico "Mario Negri", Milan, Italy, for a study of the mechanism of gossypol toxicity counteraction by L-lysine (project duration - 5 years); and Regional Cooperative for the Protection, the Development and the Practice of Fishing in Valle d'Aosta, Valle d'Aosta, Aosta, Italy, for experimental studies to elucidate the role of cottonseed meal in the induction of hepatoma in rainbow trout to obtain fundamental information concerning the suitability of cottonseed meal for use in rations for this species (project duration - 3 years).

Additional research to develop new and improved industrial products and processing technology is in progress under grants of P.L. 480 funds to the following foreign institutions: University of Montevideo, Montevideo, Uruguay, for research on the preparation, characterization, and evaluation of derivatives of gossypol for use as biologically active materials, ultraviolet absorbers, and other products (project duration - 5 years); Indian Institute of Science, Bangalore, India, for studies of the addition of carbenes to unsaturated fatty materials derived from cottonseed oil to

provide possible new outlets for utilization of the oil (project duration - 5 years); National Chemical Laboratory, Poona, India, for investigation of the synthesis and properties of new-type glycol mono alkyl ethers for control of water evaporation to extend the industrial utilization of cottonseed oil (project duration - 5 years); The Hebrew University of Jerusalem, Jerusalem, Israel, for a study of the preparation of new chemical derivatives from acrylonitrile and unsaturated fatty acids derived from cottonseed oil and other vegetable oils (project duration - 4 years); and the Hebrew University Faculty of Science, Jerusalem, Israel, for an investigation of metalation reactions for the modification of mono- and dienoic fatty acids to provide increased functionality, thereby leading to possible new industrial applications for cottonseed and other vegetable oils (project duration - 5 years).

The Federal in-house scientific effort devoted to research in this area totals 49.7 professional man-years. Of this number 22.3 is devoted to chemical composition and physical properties, 14.2 to new and improved food products and processing technology, 10.4 to new and improved feed products and processing technology, and 2.8 to new and improved industrial products and processing technology. The domestic contract and grant research involves an additional 7.5 man-years, 3.0 being on chemical composition and physical properties, 0.9 on new and improved food products and processing technology, 1.9 on new and improved feed products and processing technology, and 1.7 on new and improved industrial products and processing technology. P.L. 480 research involves 12 grants, of which 5 are on chemical composition and physical properties, 2 on new and improved feed products and processing technology, and 5 on new and improved industrial products and processing technology.

PROGRAM OF STATE EXPERIMENT STATIONS

Station research on cottonseed utilization is directed mainly toward increased feed use of the oilseed proteins. Efforts to increase the wholesomeness of cottonseed meal is centered on aspects of the gossypol and cyclopropenoid problems related in part to toxicity and in part to nutritional adequacy. When protein quality is poor, usually the lysine in the protein has combined chemically with sugars, fatty materials, or, in the case of cottonseed, with gossypol. Studies are in progress designed to determine the extent to which lysine, or possibly arginine or glutamine, has reacted. The investigations are aimed to better understand the reactions which interfere with proper utilization. High quality proteins in the rations of swine and poultry decrease costs.

Experiments designed to elucidate the effects of proteolytic enzyme action on gossypol-protein complexes have revealed purified, stable peptide end products which contain gossypol bound through lysine. Laboratory syntheses of cyclopropenoids and polymerization of sterculic acid have been examined. Methods of destroying the cyclopropene ring are being investigated. Studies on the structure of the cottonseed pigment gossyverdurin are proceeding.

Other studies include work on developing suitable methods and techniques for handling chemical residues of harvest aids in cottonseed.

The quality of cottonseed is affected by some mechanical damage during ginning, and the feasibility of storing seeds from one planting season to the next in normal warehouses is being related to viability and vigor. Changes in the composition of fatty acids resulting from the reuse of cottonseed oils for deep fat frying is being investigated. Additional studies on the roughage value of cottonseed hulls in dairy cattle feeds are being examined as a partial substitute for alfalfa hay.

The total research on the utilization of cottonseed products amounts to approximately 3.9 professional man-years.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Chemical, Physical, and Biological Properties and Structural Factors of the Proteins. The composition, properties, structural factors and reactions of oilseed proteins and associated materials are being investigated in a program of pioneering research conducted by the Seed Protein Pioneering Research Laboratory. The fundamental information developed should lead to new concepts and possibly new applications for oilseed proteins, including cottonseed protein. Since peanuts were found to be an especially suitable experimental material and employed for much of the early pioneering research on seed proteins, the report of progress in the research is given in Area No. 7, "Peanuts Processing and Products," as in the previous report.

A fundamental investigation of the physical and physicochemical properties of pure isolated cottonseed proteins is being conducted under a P.L. 480 project at the Institute of Biological Chemistry, University of Rome, Italy. A monodisperse major protein component has been isolated from the protein extracted from a glandless variety of cottonseed. This protein, called Acalin A by the investigators, has been characterized through amino acid analysis employing different methods of hydrolysis, end group analysis, dissociation into subunits of lower molecular weight, and solubility under different conditions. A second major protein which appears to differ from Acalin A has also been isolated from a glandless cottonseed extract, and has been purified to about 90% homogeneity in the ultracentrifuge. This component is currently under investigation. Some of the enzyme systems, including a transaminase, a glutamic dehydrogenase and a proteolytic enzyme, have also been isolated and studied. Such information is needed in the potential application of cottonseed proteins to human food needs (UR-E15-(40)-33).

2. Chemical and Physical Properties of Cottonseed Pigments. In the contract research at the University of Tennessee on gossypol esters and mild oxidation products of gossypol and its derivatives, mild oxidation of tetramethylgossypol diacetate with chromic acid in acetic acid was found to

yield a new binaphthaquinone in 25% yield. Reactions of the binaphthaquinone will be investigated. The structure of the binaphthaquinone obtained when gossypol is oxidized with ferric chloride was also established. This quinone was converted to its tetraacetate, and the NMR and IR data obtained support the proposed structure. Anil derivatives of this quinone and its tetraacetate were obtained and characterized. The reaction which occurs when gossypol is dissolved in ethyl alcohol was also established in recent work. This basic research offers promise of applications to improve the color of cottonseed oil and the quality of meal, and should be of value in studies of the physiological effects of gossypol in animals ingesting cottonseed products. Future plans include investigation of the oxidation of gossypol under mild, nonalkaline conditions. (S4 1-103(C)).

3. Chemical, Physical, and Biochemical Properties of the Oil and Fatty Acids, Including Cyclopropene Fatty Acids. Excellent progress has been made in several lines of in-house research on the physiologically active fatty acids, called cyclopropenes, which are present in cottonseed oil and are believed to be responsible for various abnormal effects in animals fed rations containing cottonseed products. These investigations are continuing.

Several reliable, sensitive methods of analysis by which the presence of these unique fatty acids can be determined quantitatively in various types of cottonseed oils and concentrates have been developed. For the first time, accurate analysis can now be made of concentrates even in the presence of large amounts of interfering substances. A semimicro method, adapted from the previously developed macro hydrogen bromide titration procedure, has been developed to determine cyclopropenes in cottonseed oils. A method was also developed for the quantitative determination and isolation (as methyl esters) of the residual lipids in cottonseed meals, the first phase in the development of an analytical method for cyclopropenes in such meals.

Progress has been made on the isolation and concentration of the cyclopropene acids from commercial cottonseed oils, so as to determine exactly what types are present and to enable a study of possible physiological effects. Evidence has been obtained that malvalic and sterculic acids are the only cyclopropenes in the oil; they appear to be present in an 88:12 ratio. A systematic investigation of the concentration of cyclopropenes in the methyl esters of cottonseed fatty acids by fractional crystallization was conducted. For all the cyclopropenes to appear in the filtrate fraction, esters containing 0.66% cyclopropenes could not be crystallized from a 10% solution in methanol below about -60°C. Crystallization at -60°C. yielded fractions containing about 8% cyclopropenes. In the further concentration of the methyl ester fractions, countercurrent liquid-liquid fractionation appeared to be most suitable: relatively simple fractionations yielded concentrations containing as much as 64.5% cyclopropenes. Methyl sterculate derived from Sterculia foetida oil yielded fractions containing up to 90% methyl sterculate. Feasibility of employing this process on a larger scale will be investigated.

Several effective treatments for removing or inactivating cyclopropenes in cottonseed oil were developed in recent work -- in particular, treatment with monofunctional fatty acids has aroused considerable industrial interest. Six oils were treated with acids (acetic, capric, citric, oxalic, phosphoric, and mixed cottonseed fatty acids), another was partially hydrogenated, and still another was treated with SO_2-Al_2O_3; all treatments were effective in eliminating the major adverse effects on eggs produced by hens that had ingested normal cottonseed oil. The process of inactivating cyclopropenoids in cottonseed oil by simple heat treatment during the deodorization with monobasic acids, such as mixed cottonseed fatty acids, could be an important step in solving the cyclopropene problem, but additional research is needed.

In other research, efforts are being made to employ the organism, Tetrahymena pyriformis, as a reagent in determining if cyclopropene acids have an influence on the basic cellular metabolism of fat. Techniques for extraction of fat and determination of the fatty acid patterns of Tetrahymena pyriformis fat have been developed. (S4 1-105).

The contractor (University of Illinois) has conducted further research on the chemical and physical properties of cyclopropene fatty acids. Trans-2-phenylcyclopropyl trimethylammonium iodide reacted with potassium amide in liquid ammonia to yield a mixture which apparently contained 1- and 3-phenyl-cyclopropenes. 1-Phenylcyclopropene-3-carboxylic acid was prepared; it gave no Halphen reaction. Methyl sterculate was prepared by transesterification of Sterculia foetida seed oil by urea clathration and low temperature crystallization. Evidence has been obtained that methyl sterculate apparently undergoes rearrangement on storage to yield mixtures of two products. Data indicate that the most probable composition of the seed oil of Sterculia foetida is: palmitic, 2%; palmitoleic, 0.4%; stearic, 1.6%; oleic, 11%; linoleic, 11%; sterculic plus malvalic, 54%. Information developed under this contract has contributed to the development of methods for determination of cyclopropenes, the recognition and determination of the products obtained when cyclopropenes are chemically modified, and the recognition of reactions of cyclopropenes of potential physiological significance. (S4 1-104(C)).

Some exploratory investigations of the effects of gas chromatographic separation on the chemical composition of fatty materials have been carried out. Based on preliminary experiments with a sample of methyl sterculate of supposedly high purity, it appears that thermal conversion products of methyl esters of cyclopropene acids are formed during gas-liquid chromatographic analysis and the cyclopropene groups are destroyed. This points to the need for further information on the behavior of fatty materials when they are subjected to elevated column temperatures in gas chromatography.

In a P.L. 480 research project now getting well underway at the Division of Food Preservation, Commonwealth Scientific and Industrial Research Organization, Ryde, New South Wales, Australia, a study is being made of the chemistry and biological effects of cyclopropenoid fatty acids that occur in cottonseed and cottonseed products. These fatty acids, malvalic and

sterculic, occur in the seeds of many plants of the Malvalic order and are known to cause adverse physiological responses when fed to several animal species. Substantial progress has been made in isolating and purifying the cyclopropene containing fatty acids from natural sources, and in labeling them with radioactive carbon by biosynthesis. Information obtained through the use of these materials in chemical and biological tests will be of value in the extensive domestic research program to assess the significance of cyclopropenoids in food and feed uses of cottonseed production. (UR-01-(40)-2).

Basic investigations of methods for correlating and predicting solubilities of homologous and analogous long-chain saturated and unsaturated fatty acid derivatives are in progress. The pure cyclohexylamine salt of tridecanoic acid was prepared, and accurate solubility curves for the salt in methanol, benzene, and acetone were obtained. As the corresponding data for the cyclohexylamine salt of heptadecanoic acid and of the even C_{10}-C_{18} fatty acids were already available, it was possible to construct isopleth plots and predict the data for the solubility of the cyclohexylamine salts of undecanoic, pentadecanoic, and nonadecanoic acids in all three of these solvents. The experimental and predicted solubility data obtained are of fundamental importance in connection with the cyclohexylamine salt method for preparing pure fatty acids free from homologs.

Highly pure stearic, petroselinic, petroselaidic, erucic, and brassidic acids have been prepared for use in this research. The accurate solubility data obtained for stearic acid in toluene overlap and agree very well with published solubility data for low temperatures. This curve of the combined data will be used as a basis for obtaining complete solubility curves for the large number of fatty acids for which data have been published on the low temperature solubility in this solvent. Solubility curves have also been obtained for stearic and myristic acids in N,N-dimethylformamide. These data will be used in obtaining, by prediction, solubility curves (1) for other members of the homologous series in this solvent by the isotherm and isopleth methods and (2) for related acids which are not homologs, by the new correlation procedure. Solubility data for a second, higher melting, polymorphic form of stearic acid has been obtained in toluene and N,N-dimethylformamide. The crystal structure of the new polymorphic form of elaidic acid was further characterized by X-ray diffraction measurements. Plans include the preparation of additional highly purified fatty acids for which the solubility in new selected solvents and solvent mixtures will be obtained. Theoretical analysis of existing and new data will be continued in an attempt to correlate solubility with other physical properties. These experimental and predicted solubility data, aside from their scientific value, are of fundamental importance in extablishing the validity and scope of the new correlation procedure. (S4 1-129).

Additional fundamental information on the chemical transformation of olefinic compounds of fats by hydroboration and subsequent reactions has been developed in contract research at Purdue Research Foundation. In a systematic study of the hydroboration of terminal olefinic compounds containing various functional groups, such as hydroxy, alkoxy, phenoxy, acyloxy, carboalkoxy, and cyano, it was found that the alkoxy and phenoxy groups do not react with the diborane during the hydroboration of the olefinic moiety. Although the acyloxy, carboalkoxy and cyano groups react with diborane, these undesirable side reactions can be reduced or eliminated by adding only the theoretical amount of diborane to short-chain or relatively long-chain substituted olefinic compounds, such as ethyl and methyl 3-butenoates, ethyl 4-pentenoate, t-butyl 3-butenoate, 10-undecenyl acetate, methyl 10-undecenoate and 10-undecenenitrile. The hydroxy group of olefinic hydroxy compounds, however, reacts preferentially to the olefinic moiety. The various organoboranes were easily oxidized to the respective hydroxy compounds by alkaline hydrogen peroxide; however, attempts to couple the organoboranes were not too successful. Since the carboalkoxyboranates could not be coupled, sterically hindered 5-butylacyloxyboranes have been synthesized to ascertain if unhindered alkylacyloxyboranes interfere with the coupling reaction.

In the hydroboration of terminal olefinic compounds containing various functional groups, disiamylborane (di-s-isoamylborane) has been found to exert more directive influence than diborane. That is, the electrophilic attack of the disiamylborane occurs almost exclusively at the terminal carbon of the olefinic moiety, whereas the diborane is less discriminating. The inductive effects of the various functional groups do not appear to be strong enough to affect the large steric requirement of disiamylborane. (S4 1-112(C)).

In P.L. 480 research at the British Food Manufacturing Industries Research Association, under a project now reaching its final phases, an investigation has been conducted on the fatty acid and glyceride composition of cottonseed oil and the crystallizing behavior of some of the major components. The fatty acid composition of a number of oils from cottonseed of various origins and processing histories have been examined by several different methods. Gas-liquid chromatography yielded results nearest to the accepted true values. Fractionation by low temperature crystallization has indicated that, although cottonseed oil contains 3 major component fatty acids, only 4 out of 26 probable triglycerides occur to the extent of over 8%, and the minor component acids are very uniformly distributed throughout the glyceride components of the oil. Data obtained from lipase hydrolysis in experiments have indicated a marked tendency for the 2-position in the triglyceride molecule to be occupied by an unsaturated acid, and there is some indication of overall selectivity of linoleic over oleic acid to occupy this position in cottonseed oil. Work underway using both U. S. and Indian cottonseed oils of different mean unsaturation is expected to shed more light on this tendency. The information from this research is expected to prove useful in the selection and processing of cottonseed oils for

the commercial production of improved salad oils in optimum yields. (UR-E29-(40)-26).

In P.L. 480 research at the University of Bombay, studies are being made of the relationship of the substituent fatty acid groups to the physical properties of diacid triglycerides of certain saturated fatty acids, including those that occur normally in cottonseed oil. The diacid triglycerides that are of interest in this work are those containing one or two molecules of palmitic or stearic acid, and two or one of even-carbon saturated fatty acids of the series from acetic to stearic acid. A number of such diacid triglycerides of both the symmetrical and unsymmetrical configuration have been prepared and purified to around 99.8% purity, as determined by the most sensitive available methods. Physical properties such as melting point (of the β form), density, molar volume, refractive index, molar refractivity and viscosity have been obtained for 40 pure glycerides. The data thus obtained will be of fundamental value as the basis for the further development of fats and oils specifically tailored for special food and industrial end uses. (UR-A7-(40)-3).

4. Investigation of Occurrence, Determination, and Properties of Fungi and Toxic Fungal Metabolites Which May Develop in Cottonseed and Its Processed Products. Considerable progress has been made in research investigations of fungi and toxic metabolites which may develop in cottonseed and its processed products. Aflatoxins were detected in several commercial cottonseed meals and in kernels from seed cotton exhibiting yellow-green fluorescence on the lint. Probing experiments were conducted to obtain information on the growth of fungi and elaboration of toxic metabolites in various cottonseed products: under favorable growth conditions, high levels (500,000-800,000 ppb) of aflatoxins B_1 and G_1 were produced on autoclaved or unautoclaved, glanded or glandless seed and kernels; somewhat lower levels (60,000-100,000 ppb) on meals or hulls; and quite low levels (100-300 ppb) on lint or linters. Levels of more than 2,000,000 ppb were obtained on shredded wheat. The aqueous acetone procedure previously developed for the determination of aflatoxins in cottonseed products was improved to permit analysis of aflatoxins at levels below 1 ppb and is applicable to numerous products. A micro procedure recently developed permits aflatoxin determinations to be made on as little as one milligram of material.

Preliminary results indicate that aqueous acetone extraction will simultaneously remove aflatoxins and gossypol pigments from cottonseed before the oil is removed. Meals free of aflatoxin, low in residual gossypol, light in color, and high in available lysine have been prepared, along with light-colored crude oils equivalent to many refined oils. Work has also been initiated on the fate of aflatoxins in soapstocks. Preliminary results indicate that aflatoxins are considerably modified by commercial alkali refining. Plans include the further improvement of analytical methodology--particularly the development of objective assay--as well as preparation of better working standards, increasingly efficient removal of aflatoxins from cottonseed and its products, determination of the limiting conditions for

for elaboration of toxins in cottonseed products, and study of the possible value of cottonseed having a hard seed coat. (S4 1-116).

B. New and Improved Food Products and Processing Technology

1. New Edible Oil Products Including Confectionery Fats, Food Coatings and Other Specialty Products. Further research has been conducted to develop processes for producing improved cocoa butter-like fats from cottonseed oil. The research on confectionery fats is supported in part through a Fellowship sponsored by the National Confectioner's Association.

Substantial quantities (10 lbs.) of cocoa butter-like fat were prepared by the previously developed directed esterification process. Operating conditions were found which should be suitable for use in large-scale preparations. The reaction products consisted of about 80% of the components desired in good cocoa butter-like fats and could be further purified by a fractionation (crystallization) process to yield products having the properties desired of confectionery fats.

Preparation of a good cocoa butter-like fat by a relatively simple process of hydrogenating a stearine obtained during the commercial solvent winterization of cottonseed oil under special conditons and purifying the hydrogenation product has aroused much industrial interest and should provide a new market for a significant proportion of cottonseed oil. Several firms are investigating potential commercialization of the new process. Eight hydrogenation runs on the stearine showed that a 4- to 8-fold scale-up in the batch did not affect the results, nor did the absence of solvent under the conditions used so far. The hydrogenation products, which were crystallized from petroleum ether or commercial hexane to remove most of the high-melting portion, all contained a large proportion of good cocoa butter-like fat.

A series of extractions was made to determine the best solvents and temperatures to use for removal of most of the high-melting portion from the hydrogenation product. This extraction procedure showed that the point of complete melting of the cocoa butter-like fat may be controlled by the temperature at which the solvent fractionation is conducted, but that changing the point of complete melting does not change the beginning of melting. (S4 1-125).

New and improved techniques for preparing useful derivatives of cottonseed and peanut oils by esterification and interesterification are bing investigated. It has proven possible to effect direct esterification of amylose with palmitic acid by dissolving the amylose in dichloroacetic acid and reacting with excess fatty acid in the presence of 0.4% p-toluenesulfonic acid catalyst and boiling hexane. The products contained 54-56% combined palmitoyl groups (about 0.83 D.S.), but yields were only 20-25%. Other catalysts tried were less effective. Diglycerides such as distearin, diolein, dilaurin, and dicaproin were prepared and purified so that the

course of their catalytic esterification with fatty acids could be determined. Equimolar quantities of diglycerides and fatty acids were reacted under catalysis while heptane vapors were passed through the mixture. This series of reactions showed that interesterification occurs during the first few minutes of the reaction; to help minimize it, moisture must be removed from the reactants more efficiently than in these tests. An increase in the flow rate of heptane vapors passed through the reactants also decreased interesterification. The data obtained thus far indicate that more interesterification occurs than found by previous investigators. To establish the effect of temperature on the rate of esterification and the occurrence of interesterification, a reaction at 140°C. was conducted. The efficiency of various catalysts, mostly of the sulfonic acid type, is being evaluated, and some refinements in purification and analytical procedures have been achieved. (S4 1-128).

Development of fat emulsions having increased stability and good physiological properties should facilitate their adoption for intravenous nutrition and improve the prospects of utilization of cottonseed oil in such emulsions. Such research is being conducted cooperatively with the U. S. Army Medical Research and Nutrition Laboratory and research groups from several medical schools and is supported by the Office of the Surgeon General. Although emulsions of (a) commercial cottonseed salad oil (SR 152), (b) this oil washed with ethanol-water, (c) a commercial refined-bleached-winterized cottonseed oil washed with ethanol-water and laboratory-deodorized and (d) soybean oil (SR 151) gave satisfactory performance in long-term physiological evaluations, they caused undesired decreases in blood pressure of dogs. An investigation of the cause of this was therefore initiated. Since it was found that emulsions of cottonseed oil from glandless seed produced only mild effects on blood pressure it is presumed that the pigments and polar components present in conventional cottonseed oils are responsible for the adverse effects on blood pressure. Consequently, fractionation of commercial cottonseed salad oil by column chromatography was investigated as a method more effective than washing for removal of the objectional constituents. Results indicate that a combination of bleaching earth and alumina removed essentially all of the polar materials and most of the pigmentation. Emulsion SR-188 prepared with the fractionated oil was tested for blood pressure effects and found to be comparable to the emulsion prepared with the oil from glandless cottonseed. Long-term physiological evaluations of SR-188 are now in progress. Improvements in the method of removing pigments and polar materials from cottonseed oil are being sought. (SU-0-0-2(SG)).

2. Processing Technology Related to Improved Oil Products, Including Modifying or Eliminating Cyclopropene Acids in Cottonseed Oil. Plant-scale tests conducted on the alumina bleaching process for off-colored cottonseed oils have demonstrated the feasibility of the process for commerical use. Despite the use of existing refinery equipment poorly adapted for the process, the tests on bleach-resistant refined oil showed the superiority of alumina bleaching over bleaching with the best grade of acid activated

clay. Treatment with 2% and 4% of activated alumina gave bleached oils having Lovibond red colors of 3.1 and 2.2, respectively, as compared to colors of 3.4 and 2.8, respectively, by treatment with equal quantities of activated earth. Subsequent laboratory tests have shown that in properly designed equipment, using the same oil and alumina, a bleached oil color of 2.5 red is obtainable with 2.0% of alumina and a color of 1.6 red with 4% of alumina. Close cooperation is being maintained with the major vegetable oil producer and processor who conducted the plant-scale evaluations of the process.

Recent laboratory experiments indicate that the bleaching efficiency of alumina gel precipitated from aluminum sulfate with sodium hydroxide is significantly greater than that of any commercially available alumina. Also, "Baymal"--a special fibrillar colloidal boehmite alumina--used in conjunction with activated alumina gave even better results, reducing the color of a 6.6 red oil to 0.3 red. Of several chemicals employed in conjunction with activated alumina, sulfurous acid was the most effective in reducing malvalic acid content of cottonseed oil; however, the reduction was only 80%. (S4 1-114).

Further progress has been made by the contractor (University of Illinois) on chemical investigations of cyclopropenoids to develop means of eliminating or physiologically inactivating these type constituents present in cottonseed products. Structural analysis of the three major pigmented compounds isolated from the Halphen-test reaction of 1,2-diethylcyclopropene has continued. One of the compounds was identified as cis-1,5-diethyl-2,4-dithiobicyclo(3.1.0)hexane-3-thione. A second compound has been tentatively identified as a resonance hydrid of 1,2-diethylcyclopropyl 5-ethyl-3-(thioacetyl)-1,2-dithia-3,5-cyclohexadien-6-yl thioether and 1,2-diethylcyclopropyl 2-ethyl-4,5-cyclodithia-2,4-hexadienedithioate. The third compound has not yet been identified.

In other studies of the chemistry of cyclopropenoids by the contractor, the cyclopropene moiety of sterculene (1,2-dioctylcyclopropene) was partially protonated and cleaved when refluxed for five hours with benzene and acetic acid, but a small amount of perchloric acid greatly increased the speed of the reaction, even at room temperature. In both cases, the reaction products contained 9-methylene-10-acetoxyoctadecane, 9-methylacetoxy-9-octadecene, and 9-methyl-10-acetoxy-9-octadecene. The perchloric acid-catalyzed reaction also produced a small quantity of 9-methylacetoxy-10-octadecanone. It was found that formic acid will slowly protonate and cleave the cyclopropenoid moiety of sterculene at room temperature in the presence of an aqueous hydrogen peroxide or perchloric acid catalyst. Similar type acyloxy derivatives described above are obtained; but, in addition, the hydrogen peroxide catalyst causes the formation of 9-methylene-10-octadecanone. Based on these fundamental findings, Halphen-negative cottonseed oil was prepared by reacting 100 milliliters of cottonseed oil, 10 milliliters of acetic acid, and 1 milliliter of perchloric acid at room temperature for 2 hours. The oil was slightly brown after treatment.

A sensitive photometric procedure developed for the analysis of small quantities of cyclopropenoids could prove useful for assaying cottonseed oil for its cyclopropene content. (S4 1-107(C)).

3. Cottonseed Flours and Derived Products for Human Consumption in Developing Countries. A recently initiated study of the preparation of cottonseed flours and their derived products for human consumption in developing countries, which is supported by the Agency for International Development (AID), has produced some promising results. Current research is being directed to developing simplest types of screw pressing and solvent procedures, including 2-stage extraction processes, suitable for small or medium size extraction plants to produce defatted or partially defatted flours. Four of the procedures have been used on a bench-scale to prepare small lots of cottonseed flour, which were submitted to the Human Nutrition Division to be evaluated in biscuits, noodles, tortillas, unleavened bread, yeast bread, and cookies. Preliminary results indicate improvements are probably necessary in flavor and color for the yeast breads and perhaps other products. Two larger lots of cottonseed flours have been made in the pilot plant for UNICEF using the hexane-acetone-water mixed solvent extraction process. One is being evaluated in Peru as the sole source of protein in infant feeding over an extended period of time and results show it is practically equivalent to milk protein. UNICEF is presently having these flours evaluated in Peru, Egypt, Italy, Guatemala, England, and other countries, as well as in the U. S. A. The flours are high in protein and available lysine content, low in fiber, low in free and total gossypol, and show no detectable amount of aflatoxin. Pilot-plant scale equipment is currently being procured and assembled in an enclosed area to enable the production of the flours under sanitary conditions. (SU-0-0-3(AID)).

C. New and Improved Feed Products and Processing Technology

1. Basic Research to Improve Nutritive Value of Cottonseed Meal for Poultry and Swine, Including Investigations of Physiologically Active Contituents. As a basis for improving the nutritive value of cottonseed meal (and flour), research is continuing on the chemical composition and characteristics of the protein systems of cottonseed. Completed analyses of the amino acid and fatty acid constitutents of the species of Gossypium that can be induced to cross with upland cotton show that there is no amino acid or fatty acid pattern characteristic of the genus. Significant range between species has been encountered in the limiting amino acids and in the major fatty acids. This knowledge provides an opportunity to modify genetically the composition of commercial cottonseed to improve the nutritive value of the meal and increase the versatility of the oil.

Other work has been directed toward obtaining a thorough understanding of the effect of lipid extraction on nitrogen solubility and the nature of the nitrogenous materials of cottonseed. It was found that hydration of cottonseed before defatting decreased the percent lipid extracted by non-polar solvents but had no effect on the percent nitrogen extracted by water from the defatted material. Hydration increased the percent non-nitrogenous

materials extracted by polar solvents or solvent mixtures, producing a protein concentrate, but decreased the percent nitrogen extractable by water from the defatted material. Gel electrophoresis demonstrated the presence of ten major protein components in the water soluble fractions at pH 6.8 or 8.7. Evidence was obtained for the presence of a proteolytic system which selectively hydrolyzed two of the ten components.

The Sephadex G 200 profile of the water soluble portion of defatted cottonseed in pH 8.9 buffer, using the Lowry procedure for measuring protein, was arbitrarily divided into six fractions. Gel electrophoresis of the fractions substantiated the fractionation of the protein components, the major portion of which are found in Fractions III, IV and V. Fraction VI, a major Lowry positive fraction, was shown by dialysis, ninhydrin, and anthone tests to be composed of free amino acids, peptides and carbohydrates. Hydration of the seed before defatting with the same solvent decreased Fractions II and III of the Sephadex profile and changed the amino acid profile. Cystine and the basic amino acids increased, and valine, isoleucine, and leucine decreased in the water soluble fractions. The native enzymatic activity in the water soluble fraction, demonstrated under sterile conditions, causes a major decrease in Fractions II, III, and IV and a concurrent increase in Fraction VI in the Sephadex profile after incubation in pH 6 Tris buffer for 72 hours. Ten meals have been prepared from quiescent and hydrated glandless seed by batch extraction with polar and nonpolar solvents for nutritive evaluation in cooperation with the Ralston Purina Company. A trainee supported by UNICEF has participated in this research. (S4 1-130).

Investigations to isolate and identify the factors in cottonseed meal that cause mortalities among swine have continued, in cooperation with the Pharmacology Laboratory at WU, the Animal Husbandry Research Division, ARS, and the Ralston Purina Company. The rate of growth of swine receiving cottonseed meals as their protein supplement in rations based on cereals may be predicted satisfactorily on the basis of available lysine in the meal proteins, but this test is not satisfactory since mortalities occur among swine receiving certain cottonseed meals without there being a correlation between the deaths and the protein quality of the meals. Several cottonseed meals causing mortalities in swine feeding experiments were fed to protein-depleted rats, but produced no indication of toxicity. The protein efficiency ratio, as determined in the protein-repletion tests on rats, ranged from 1.17 to 1.93 for commercial cottonseed meals and from 2.58 to 2.74 for the cottonseed meals prepared by acetone-hexane-water solvent extraction, as compared with a value of 2.45 observed for a selected soybean meal. Analyses of tissues of rats that have received cottonseed meals lethal to swine were continued, but no conclusions have been reached.

Feeding swine soybean meal combined with gossypol in different treatments has indicated that the physiological activity depends on the manner in which the combination takes place. Total gossypol found on analysis of the soybean-gossypol complex is always less than the quantity of gossypol added. The nature of the combination of gossypol and meal constituents that gives rise

to physiologically active gossypol derivatives has not been determined.

Albumin components of egg white proteins migrated into the yolk through the blastoderm of eggs produced by hens ingesting soybean meal-cottonseed pigment gland mixtures. Abnormalities in the eggs produced by such hens included pH change in the yolk and whites, but not the fatty acid patterns of the yolk fat. It appears that a good estimate of the value of a cottonseed meal for broiler rations may be obtained from a knowledge of the available lysine level. Some sources of error in the published method for determining available lysine have been identified; at the 1% level of probability, the confidence limits for reproducibility are $\pm$ 8 parts in 375. (S4 1-110).

2. Processing Technology Directed Toward Improving Meals. An investigation recently initiated is designed to determine processing conditions for the production of oils and meals of maximum quality from glandless cottonseed, in cooperation with the National Cottonseed Products Association; the Human Nutrition Research Division, ARS; and UNICEF. This type of cottonseed, from which gossypol has been removed genetically offers an outstanding opportunity to the cottonseed industry to improve the quality of its products and to expand and strengthen markets. A lot of 4,400 pounds of the glandless seed was solvent-extracted to produce about 1,200 pounds of low-lipids and high-lysine content meal. Mixed solvent was used for this extraction to insure simultaneous removal of approximately 6 parts per billion mycotoxin found to be present in the meats. The meal will be ground to flour, sterilized at 180°F. and shipped to Guatemala for experimental use in human food formulations. Bench-scale equipment is being assembled to determine optimum preparation, extraction, and desolventization conditions for processing glandless cottonseed by screw-pressing, prepress extraction, and direct extraction. Various extraction methods and various solvents will be studied. Parallel studies will be carried out with glanded seed, which are known to require limited use of heat and moisture in processing because of the deleterious effects of gossypol on both oil and meal or flour quality. (S4 1-127).

The inactivation or removal of aflatoxins from contaminated cottonseed and its products is requisite to their being used in feeds (and foods). Treatment with chemicals, especially those based on ammonia, appear to be effective in reducing the aflatoxin content of contaminated cottonseed meals without significantly altering their nutritive value. Cottonseed meal containing 145 ppb of aflatoxin B_1 was treated with 5% by weight based on the meal of the following reagents by themselves and in combination: Ammonium salts (carbonate, acetate, chloride), urea, calcium hydroxide, and sodium sulfite. Four reaction conditions were used which varied time, temperature, amount of water used, and the type of vessel, i.e. open with stirring vs. closed. Control reactions (no reagents used) under all conditions reduced the aflatoxin B_1 to 74-80 ppb. The most effective treatment appeared to be a mixture of sodium sulfite and ammonium chloride, yielding a product containing 27 ppb of B_1. Ammonium carbonate and calcium hydroxide appeared less effective (36 ppb) under the best treating conditions. Addition of urea had no effect. A mixture of soyflour and cottonseed meal (1:2 ratio) after

heating with added moisture yielded a product containing 36 ppb. Anhydrous ammoniation also produced good results with cottonseed meal: this treatment reduced the aflatoxin content from 145 ppb B_1 to no detectable B_1. Future work will be directed toward developing practical methods for inactivation of aflatoxin by chemical treatments, especially those based on alkalies. Feeding studies will be conducted in cooperation with WU and other groups to better define the conditions required for destruction of aflatoxin without impairing nutritive value. (S4 1-133, Pending).

Contract research is being conducted by the Illinois Institute of Technology Research Institute to develop practical processing methods for inactivating cyclopropene groups in cottonseed meal. The development of an accurate and sensitive procedure for detecting low levels of residual cyclopropenoid fatty acids (CPA) in cottonseed meals is essentially complete; this analytical procedure furnishes an essential research tool for determining the efficiency of chemical inactivation or extraction procedures. Prior research at SU aided in this development. Basically the procedure involves Soxhlet extraction of residual lipids with methanol, preparation of methyl esters in the methanol extract by transesterification with sodium methoxide, isolation and purification of methyl esters to remove interfering pigments, followed by spectrophotometric determination of CPA by use of a sensitive Halphen reaction. As little as 1×10^{-4} grams of CPA can be detected by the Halphen reaction. Typical commercial cottonseed meals were found to contain residual CPA ranging from 0.001 to 0.020%. The analytical procedure should be capable of detecting levels as low as 0.0001% residual CPA in treated meals. Work has been initiated on laboratory-scale experiments to inactivate or remove residual CPA in commercial cottonseed meals. (S4 1-117(C)).

Research is continuing on the rates of extraction of oil of cottonseed with acetone-hexane-water solvent mixtures and on the properties of the resulting marcs and miscellas. Material balance studies on a 4-step countercurrent extraction of raw moist cottonseed flakes, where the vibrating screen separation procedure was used, showed that extraction of oil is very rapid and substantially complete; residual oil in the air-dried marc is reduced to a very low level by light pressing between each pass in the countercurrent extraction; and the miscellas and crude oil are relatively stable, no color fixation being noted for weeks during storage. Fines did not accumulate during continuous operation when the miscella was recycled at the third step of the process. Ten-step countercurrent extractions of raw moist cottonseed flakes with the azeotrope were also carried out in the basket centrifuge with solvent-to-flakes ratios of 3:1, 2:1 and 1.25:1. Residual oils in the final marcs were less than 0.1% for solvent-to-flakes ratios of 3:1, and 2:1, and about 0.2-0.3% for solvent-to-flakes ratio of 1.25:1. Optically clear miscellas were obtained. Total gossypol values in these marcs (air-dry basis) ranged from 0.1 to 0.25%. The quantitative extraction of oil from moist raw cottonseed flakes can be achieved with azeotrope in a continuous extraction with a residence time of about 3 minutes. Use of the mixed solvent should point the way to a greatly improved processing method for oilseeds, and the superior nutritional quality of the cottonseed meal should lead to its

increased utilization in swine rations. (S4 1-123).

D. New and Improved Industrial Products and Processing Technology

1. Research to Develop New Reactions and Products Suitable for Industrial Use. Nineteen additional symmetrical N,N-disubstituted long chain amides were prepared, characterized, and evaluated as plasticizers for polyvinyl chloride and will be submitted for antimycotic-activity screening. Plasticizer performance has now been determined for the N,N-dibutyl amides of a number of pertinent long chain fatty acids including palmitic, stearic, linoleic, ricinoleic, erucic, epoxystearic and dimer acids, as well as Armour "animal acids" and parsley seed acids, rapeseed acids, Limnanthes douglasii seed acids, and selectively hydrogenated cottonseed acids. All except the stearic, linoleic, and ricinoleic acid derivatives passed the 30-day shelf-storage compatibility test. In general these amides are more efficient than DOP, and most of them, including those of the seed oil acids and "animal acids," gave very low brittle points, ranging between -51 and -63° C. They are thus comparable to dioctyl adipate (-55° C.) without the objectionably high volatility loss of the latter. Fifteen other long chain N,N-disubstituted amides, most of which were unsymmetrically N,N-disubstituted oleamides, were also prepared and evaluated. All passed the compatibility test.

The plasticizing characteristics of the various derivatives that contained one 2-acetoxyethyl substituent did not differ appreciably from those of the symmetrically disubstituted N,N-bis(2-acetoxyethyl)oleamide. The N,N-bis[2-(3-formylpropionyloxybutyl)ethyl] and N,N,-bis[2-(3-formylpropionyloxyhexyl)ethyl] oleamides gave somewhat less satisfactory low temperature performance than the N,N-bis(2-acetoxyethyl) derivative but were more resistant to soapy water extraction. Exploratory experiments have markedly improved the commercial attractiveness of such plasticizers by showing that an efficient stabilizer can be prepared. A commercially available dibutyl tin mercaptide stabilizer used in conjunction with an alkylarylphosphite chelator provided excellent thermal stability to polyvinyl chloride resins plasticized with N,N-dibutyloleamide.

Twelve trial compositions (4-propylpiperidides and mixed 2-methyl-3(5)ethylpiperidides of six commercial fatty acids) were evaluated as polyvinyl chloride plasticizers for a chemical company to assist them in selecting the best ones for preparation on a pilot-plant scale for test marketing. The two compositions rated best were made from the cheapest fatty acids; one of these will soon be sample-distributed by the company and in large volume will be competitive in price with DOP. These commercial evaluations have resulted largely from earlier SU research on piperidides of long-chain fatty acids. (S4 1-124).

Contract research sponsored jointly by SU, NU, EU and WU seeks to extend the industrial utilization of agricultural products in commercial plastics through an investigation of the free-radical high-pressure copolymerization of ethylene with unsaturated fatty acids and other selected, commercially

available agricultural monomers. The contractor (U. S. Industrial Chemicals Corp.) has completed copolymerization runs at three ranges of comonomer concentration (3%, 10%, and the maximum feasible) for methyl oleate, methyl undecenoate, methyl esters of the acids of tung, castor, dehydrated castor, safflower, conjugated safflower, and linseed oil. Maximum concentration of monomers for stable reaction was 31, 40, 15, 29, 26, 24, 20, and 19, respectively. The more unsaturated or the conjugated monomers adversely affect the concentration and efficiency of the catalyst. Although the less unsaturated monomers produced more interesting products, the molecular weight of all products was too low to permit use as blown film; some, however, may offer promise for less concentional plastics applications. Plans include the polymerization of ethylene with vinyl laurate and erucylamide and further evaluation of the more promising monomers. (S4 1-115(C)).

Research under another contract (University of Arizona), also sponsored jointly by the four Divisions, has produced considerable information on the polymerization of vegetable oil derivatives for use as elastomers, plastics, thickening agents, or protective coatings. Samples of copolymers of vinyl esters of nonhydroxy carnauba wax acids and of pure saturated C_{18} cyclic vinyl esters, supplied by NU, with vinyl chloride were prepared for evaluation. The vinyl ester of the cyclic acid obtained by the addition of ethylene to tung oil has also been prepared and purified by reprecipitation for determination of physical properties. Research on the polymerization of monomers from fats will be continued under a new contract. (S4 1-89(C)).

A fundamental investigation of the chemistry of gossypol and its derivatives having potential industrial utility is now nearing its final stages in a P. L. 480 research project being conducted at the University of Montevideo, Uruguay. A large number of derivatives of gossypol, many of which have not been heretofore reported, have been prepared and characterized. Among these are 24 new imino derivatives, 8 new ester derivatives, along with cyanohydrin and hydantoin compounds. Derivatives have been screened for potential usefulness as fungicides, germicides, ultraviolet screening materials and as potential anti-cancer agents. Gossypol, the yellow primary pigment of cottonseed, can be made readily available by isolation from byproducts of cottonseed oil refining. The information gained in this project may indicate promising industrial or other uses for this chemically reactive natural pigment. (UR-S9-(40)-2).

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AREA NO. 7 - PEANUTS PROCESSING AND PRODUCTS

Problem. Peanuts constitute a major cash crop in the Southern States and are in surplus. Because of their high price the domestically produced peanuts are used primarily (currently about 63 percent of the crop) in foods such as peanut butter, confections, bakery goods, and roasted and salted nuts. A critical problem in the utilization of peanuts, which has recently been made more clearly evident, is the sporadic contamination of peanuts by toxin-producing strains of common molds. The possibility of toxins entering foods intended for human consumption, as well as feedstuffs, is of the utmost concern. Intensified research is therefore urgently needed on the isolation, identification, evaluation, control, and inactivation or removal of mold toxins such as aflatoxin which may develop in peanuts and processed peanut products. New type food products and improvement in the quality and uniformity of existing products are needed to increase consumer acceptance and extend markets for peanuts; the average per capita consumption has been rather stable since World War II. The increased trend toward mechanical harvesting has necessitated the use of artificial means for curing and drying peanuts, with the result that processed peanuts and peanut products do not always possess the same desirable flavor and physical properties as peanuts which have been cured slowly in the field. Information is needed as to the physical and chemical characteristics of those chemical constituents in peanuts which affect flavor, aroma, and other important properties of the processed products, as a basis for developing new or improved products and processing procedures. Fundamental studies of peanut proteins and associated materials could similarly lead to the development of new concepts and new uses.

USDA AND COOPERATIVE PROGRAM

The Department has a continuing long-term program involving organic chemists, biochemists, analytical chemists, a microbiologist, and chemical engineers engaged in both basic and applied studies on peanuts and peanut products to increase consumer acceptance and extend markets for peanuts.

Research to develop basic information on the chemical composition and properties of peanuts, its constituents, and processed peanut products is carried out at New Orleans, Louisiana. As a part of the Seed Protein Pioneering Research Laboratory's research on various seed proteins, fundamental investigations of peanut proteins and associated materials are conducted to form the basis for developing new concepts and perhaps new uses for peanuts and peanut proteins. In other in-house research, peanut constituents and their modification by processing that influence nutritive properties and consumer acceptance of processed peanut products are studied. Current phases of this research include investigations of the lipid or lipid-soluble constituents of peanuts and processed peanut products involved in the genesis of peanut flavor and aroma; and isolation, identification,

evaluation and control of fungi and toxic fungal metabolites which may develop in peanuts and its processed products. The Crops Research Division of ARS, the Consumer and Marketing Service, and several State Experiment Stations cooperate in the research by providing samples of peanuts of known variety and history. The Pharmacology Laboratory at the Western Regional Research Laboratory, Albany, California, and the Food and Drug Administration cooperate in certain biochemical aspects of the research.

Additional research on chemical composition and properties is being carried out under contract at Evans Research and Development Corporation, New York, N. Y., on the isolation, identification and characterization of flavor and aroma components of processed peanut products; at the Agricultural Experiment Station, Oklahoma State University, Stillwater, Oklahoma, on a study of the relation of the carbohydrate, amino acid and protein components of the peanut to the formation of flavor and aroma during roasting; at the Agricultural Experiment Station, Auburn University, Auburn, Alabama, on a study of the limiting environmental conditions for the elaboration of mycotoxins in peanuts; and at the Agricultural Experiment Station, Texas A&M University, College Station, Texas, to develop information relating processing methods, preprocessing history, distribution of immature, mature and germinating peanuts, and external conditions such as mold incidence as they affect consumer-use properties of processed peanut products.

New and improved food products and processing technology are being developed in research conducted at New Orleans, Louisiana. One important line of research is concerned with the development of economically feasible methods for the inactivation or removal of aflatoxins from contaminated peanuts and peanut products to permit their utilization in foods (and feeds). Cooperation is maintained with the Crops Research Division, ARS, Market Quality Research Division, ARS, State Experiment Stations, the Pharmacology Laboratory of WU, the Food and Drug Administration, industry, and nutritionists in USDA, at universities and elsewhere, in connection with this research. Other research, supported by the Agency for International Development, involves a study of the preparation of peanut flours and their derived products for human consumption in developing countries. Cooperation is maintained with UNICEF for arranging nutritional evaluations of experimental products in developing countries, and with the Human Nutrition Research Division, ARS, for evaluating certain of the products. Other research is concerned with the development of low-fat peanuts having acceptable peanut flavor and texture characteristics. The possibility of removing aflatoxin, if present, by applying certain treatments during processing will also be determined in connection with this work. Informal cooperation is maintained with peanut suppliers and processors, and with nutritionists and home economists for evaluation of experimental products as required.

Additional research on new and improved food products and processing technology is being carried out under contract at the Agricultural Experiment Station, Auburn University, Auburn, Alabama, on the development of peanut products for use in preparation and fortification of processed and

convenience foods; and at the Agricultural Experiment Station, Oklahoma State University, Stillwater, Oklahoma, on a study of sterilizing or inactivating treatments in conjunction with artificial drying and curing of peanuts to develop processing conditions needed for producing mycotoxin-free roasted peanut products of optimum quality.

The Federal in-house scientific research effort in this area totals 14.4 professional man-years. Of this number 7.6 is devoted to chemical composition and physical properties and 6.8 to new and improved food products and processing technology. Contract research involves an additional 5.8 man-years, 4.1 being on chemical composition and physical properties and 1.7 being on new and improved food products and processing technology.

PROGRAM OF STATE EXPERIMENT STATIONS

State stations have a continuing program of research aimed at discovery of new uses for peanuts. In recent years a portion of this program has been directed to fundamental studies on the fermentation products produced by fungi growing on peanut substrates. During the past year, this work has been expanded to include determination of the sources and prevalence of fungi responsible for mycotoxin development in Southwest Spanish peanuts. The effect of field damage on subsequent infection by toxin elaborating fungi is being evaluated in relation to curing, handling, and marketing methods. Attention is also being given development of methods for preventing mycotoxin elaboration during post-harvest processing and marketing.

With the inception of mechanized harvesting and curing processes for peanuts some 15 years ago, the problem of "off-flavors" in raw and processed peanuts and peanut products has been of increasing concern to the industry. Several stations are investigating the source(s) and cause(s) of objectionable flavors in peanuts. For example, the type of off-flavor which arises when uncured peanuts are subjected to high drying temperatures is distinctive. Investigations have shown that levels of this off-flavor development in peanuts is a function of the curing temperature, time of exposure to heat, moisture content, and stage of maturity of the kernels. Some 21 volatile compounds have been isolated from this type of peanuts.

Other composition studies seek to determine the factors in peanuts which are responsible for the differences in susceptibility to various types of oxidative rancidity development. Work is also continuing on effects of production practices and storage conditions on the chemical, biochemical and physical changes which occur in peanuts and the relationship of these changes to odor, flavor and nutritive factors.

Studies on the flavor and aroma of peanuts involve consideration of the agronomic and biochemical factors responsible for the flavor of peanuts and peanut butter. Attempts to characterize the substances responsible for the aroma and flavor developed on roasting continue. Efforts to identify and quantitate the components of the aroma fraction have resulted in

identification, by gas chromatographic techniques, of some of the carbonyl compounds produced when precursor fractions are pyrolyzed.

Product development work is carried out in an effort to extend the use of peanut butter, salted peanuts and peanut oil by improvement of present products or through development of new products. Variables in processing conditions are studied to determine effects on product quality. As a part of a program for using peanut protein preparations in foods to improve their nutritive quality, peanut protein fractions are being used in food formulations. Attempts are also being made to develop new peanut items for the diet. In one approach, peanuts are dried at low temperatures and the oil removed to yield lower calorie items. Other flavors are then added to further vary the characteristics of the items. Use of peanut oil meal as a source of protein for swine and chicks is being evaluated. Growth rate, feed efficiency and various carcass quality characteristics are measured.

The station program on peanut utilization involves approximately 5.3 professional man-years.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Chemical, Physical, and Biological Properties and Structural Factors of the Proteins. In pioneering research conducted in the Seed Protein Pioneering Research Laboratory, important advances have been achieved in determining the ultrastructure of quiescent seeds, in developing and improving methods of enzyme and protein research, and in studying protein synthesis in seeds.

A reliable and versatile methodology has been developed for the determination of the ultrastructure of quiescent seeds. With the development of the concept of aleurins (proteins contained within aleurone grains), interest has increased in determining the ultrastructure of the quiescent state of seeds and especially the conditions of the various organelles. Previous methodology had required that seeds be wetted for some period before being studied. This introduced the possibility of changes of the type which occur in the early stages of germination. It is now possible to study seeds extensively by permanganate fixation. These studies have shown the universality of aleurone grains; have shown how they develop in the premature seeds and verified the vacuolar origin of such grains; and have shown that many of the present pictures of protein bodies may be artifacts since they can all be produced in the cotton embryo by appropriate methods of fixation. In some instances lumps of electron-dense material are found in protein bodies; these are now being explained as caused by precipitation of the protein. It was shown that the mature aleurone grains contained the necessary material to dissolve their protein in a small quantity of water.

Electron micrographs of peanut cotyledon infected with Aspergillus flavus

show the micella of the organism. One of the interesting points is that the lipid particles (the spherosomes) are attacked first, leaving the aleurone grains intact in many instances.

In addition to staining with permanganate it has now become possible to stain with osmium, which reveals much more of the structure of the seeds. This has heretofore not been possible with oilseeds, but the methodology has finally been developed; the fine detail achieved by this method of staining can now be done in dry seeds as well as any other tissue.

Advances have been made in preparative electrophoresis on polyacrylamide gel to the point where the equipment is now operating routinely. Equipment for preparative electrophoresis was built, based on the experience gained with small column equipment. The new column will handle 20 to 30 milligrams of proteins at a time during a 16-hour period; it is fully automatic; maintains constant pH; maintains constant ion population in both electrode chambers; monitors and collects the effluent from the bottom of a 5 millimeter column. The same polyacrylamide gel column can be reused: columns have been used for as long as 400 hours of operating time. With such a column it has been possible to purify arachin, the major protein of the peanut cotyledon, into a fraction which migrates as a single specie on polyacrylamide gel. In so doing, a nucleic acid fraction was removed from the original preparation. It is now being used routinely to prepare adequate quantities of pure arachin for further physical-chemical and chemical studies.

The microcalorimeter designed and built at this laboratory was used to study the migration of glucose through a living membrane. With hemoglobin as a model, it has been possible to study the heat of protonation and in this way to determine the condition of the imidazole groups in the protein.

One of the problems in calorimetry is the length of time taken to equilibrate the reaction vessel. A new calorimeter was completed which uses the Peltier effect to cool the calorimeter so that one can compensate the heat produced in the actual reaction by a known amount of electrical current. This instrument has two advantages over previous ones: first, it allows one to determine more accurately the major portion of the heat; secondly, it allows for more rapid equilibration, which permits many more experiments with the same equipment and experiments with heat-labile materials.

A soluble derivative of edestin has been prepared. Edestin, the major globulin of hempseed and one of the oldest known and best studied of the seed proteins, is quite insoluble in buffers at low ionic strength and neutral pH: less than 1 milligram per milliliter is soluble under these conditions of room temperature. A method was devised to modify edestin by chemical reaction to increase its solubility. D, L-alanyl residues were polymerized onto the free amino groups of the protein. Although such a technique had worked well with other proteins, it did not work with edestin until the protein was first put into a solution of sodium dodecylsulphate (SDS), after which the polymerization reaction was conducted. Under such

conditions the solubility was increased to over 60 milligrams of protein per milliliter. There is an optimum concentration of SDS; at higher concentrations, the protein is not modified. It will now be possible to purify edestin by many of the techniques available to protein chemists and to study the properties of a homogeneous preparation of this modified protein.

A beginning has been made in studying some reactions of methionine in peptides. Methionine is more reactive than many had ordinarily considered and can be easily oxidized to the sulfoxide and sulfone. Investigations were conducted on the reaction of methionine in model systems, particularly the formation of sulfonium salts of alkyl halides.

In the course of these investigations another reaction was discovered. When the sulfonium salt is dried to remove excess solvent, there is a reaction which results in the destruction of the methionine moiety with the concomitant linkage of the substituents on the amino and carboxyl groups of methionine. One could imagine that if the same sort of rearrangement took place in the protein chain, one could remove methionine from a chain and shorten it by one amino acid, all in the same operation. Work is continuing to determine the generality of this reaction.

Seeds are an excellent model for the study of protein synthesis since many enzymes are synthesized de novo on germination. One such enzyme is lipase in oilseeds: it does not exist in seeds such as cottonseed or peanuts but is found after four to six days of germination. Even in the castor bean where there is considerable lipase activity in the resting seed, much more is developed on germination. Synthesis of this enzyme was studied in excised (distal halves) cottonseed tissue. It was found that there is a requirement for axial tissue for the synthesis to take place; the axial tissue can be replaced by gibberellic acid. Under conditions where gibberellic acid promotes the synthesis of lipase in distal halves of seeds, aflatoxin will inhibit this protein synthesis. Actinomycin D will also inhibit this protein synthesis.

There are differences among seeds. Some cottonseeds do not require gibberellic acid for the distal half to synthesize the enzyme; in these seeds, the synthesis is not inhibited by aflatoxin. Other samples of cottonseed do not undergo any synthesis in the absence of gibberellic acid; here the synthesis is inhibited by aflatoxin. A third sample was found to be intermediate between the two. It would seem that either conditions of maturation or storage cause these differences in the protein synthesis pattern.

Most of the activity of aflatoxin has been described heretofore in animal systems. The aforementioned research on protein synthesis has indicated a plant model for studying the effect of aflatoxin on protein synthesis. Moreover, this model seems to be excellent for studying the mechanism of action of gibberellic acid.

In the course of this investigation it was shown that regardless of whether

or not protein synthesis takes place, in all instances the free amino acid pool is the same. Further work showed that proteinases are present in the ungerminated cotton seed; the availability of amino acids is not a critical factor in determining the extent of protein synthesis. (SU P1).

2. Identification of Constituents and Factors Influencing Flavor, Aroma, Color, Structure, and Nutritive Value of Processed Products. In basic research, the nonglyceride lipid-soluble constituents of peanuts and their processed products are being investigated with the ultimate objective of expanding utilization. A method was sought for detecting fractions of peanut oil that may affect the development of aromas and flavors during roasting. Peanut-like aromas and flavors develop only when peanut dry matter is roasted in the presence of oil--any oil or oil-fraction tried, including USP heavy mineral oil--whereas oil-free peanut meal and flakes develop a scorched aroma when dry-roasted. Oil or oil-fractions heated alone, however, do not acquire a peanut-like aroma. Separation of the minor nonglyceridic components of peanut oil from the unhydrolyzed oil has been unexpectedly difficult. Separation of these components by methods used for extracts of animal organs has not been as effective as the literature would lead one to expect. Repeated batchwise partition between hexane and acetonitrile-methanol mixtures have been found to be more efficient for enrichment of nonglyceridic components of crude peanut oil than either batchwise adsorption and elution, batchwise partition between other solvent pairs, or continuous liquid-liquid partition. Column chromatography has been investigated further for separation of minor components of peanut oil. Silica gel columns developed with 1,2-dichloroethane containing increasing amounts of methanol have given the best separation, although most column fractions obtained to date are still mixtures. Gradient elution is less effective than stepwise elution. Milligram amounts of two microcrystalline materials have been obtained but have not been separated successfully from the accompanying oils. Crystallinity has been lost on subsequent manipulations before sufficient purification had been effected for characterization. Infrared curves of all fractions obtained in moderate purity have indicated either hydrocarbons or esters. Work on identification will be continued under a revised line project. (S4 1-109).

In contract research on the constituents responsible for flavor and aroma in roasted peanuts, conducted by Evans Research and Development Corporation, the extracts from a five-hundred pound batch of peanuts have been separated into acidic, phenolic, amine, and neutral fractions. An extraction sequence was devised whereby odoriferous acids and phenols were isolated from the methanol-soluble concentrate. The resulting acids were examined by gas chromatography, descending paper chromatography, and thin-layer chromatography of p-phenylphenocyl derivatives. Propionic, butyric, isobutyric, hexanoic, heptanoic, and lauric acids were identified, in addition to acetic and isovaleric acids, as previously reported. Other acids are evidently present; although one has been isolated as sharply melting crystals, it has not been identified. When the acidic fraction was further examined by column chromatography on silicic acid, an odoriferous material appeared as one elution peak from the columns, but paper chromatography indicated that it was a

mixture of several components.

By paper and thin-layer chromatography, at least six phenols have been shown to be present, though none have been identified. Further work with the phenolic fraction resulted in the separation of several components in small quantities. Infrared spectral data and other properties revealed that two of these appear to be aliphatic lactones rather than phenols, a development that would account for earlier failures to prepare phenolic derivatives from these fractions. An amine fraction consisting of 0.6 gm. of a brown oil has been isolated but has not yet been examined. From the neutral fraction, beta-sitosterol has been isolated and carbonyl derivatives--one of which might be a derivative of crotonaldehyde--have been separated and purified.

An attempt was made to isolate aroma precursors by a procedure involving solvent extraction, dialysis, and liquid-liquid extraction. Two fractions obtained gave aromas reminiscent of roasted peanuts when heated. One fraction, however, produced an aroma which more strongly resembled chocolate. The work on flavor and aroma components is now being extended to include the Southwestern Starr variety, a Spanish-type peanut, in addition to Southeastern peanuts. (S4 1-106(C)).

Research complementary to the preceding project is being conducted under a contract awarded to the Agricultural Experiment Station, Oklahoma State University of Agriculture and Applied Science: an investigation of the relation of the carbohydrate, amino acid, and protein components of peanuts to the formation of flavor and aroma during roasting. Peanuts of the Argentine variety, whose genetic background is known, were grown, harvested, and cured under four conditions (windrowed, and artificially at 90F, 105F, and 120F). These controlled conditions were not associated with significant differences in total oil and protein contents. However, analyses of "flavor precursor" fractions showed that higher curing temperatures greatly increased the loss of sugars, amino acids, and peptides. Representative samples were stored under three conditions (ambient, 36F, and 70F) in both the shelled and unshelled states. Data were recorded on irrigation; daily precipitation; temperatures during the growing period; and curing, comprising temperatures, relative humidities, and kernel moisture contents. Evaluation of methods for estimating maturity revealed that two proposed methods--screen size and pod characteristics--were unsatisfactory. Efforts will be made to correlate the organoleptic and chemical parameters with curing and storage conditions, data which are valuable in selecting the optimum environment during these important stages of processing. (S4 1-119(C)).

3. Investigation of Occurrence, Determination, and Properties of Fungi and Toxic Fungal Metabolites That May Develop in Peanuts and Their Processed Products. Several projects have been initiated to investigate different facets of the problems generated by contamination of peanuts by mycotoxins, a development of major importance to the peanut industry. A number of these facets were studied in the first project.

First a survey of the prevalence of aflatoxin in peanut stocks held by CCC was made on 112 samples from 16 warehouses in five states, representing three types and four grades. Aflatoxin was present in peanuts from all areas; although the aflatoxin content of peanuts from various geographical locations was not demonstrably different, there was a decided difference among grades. The amount of aflatoxin B_1 ranged from 3 to 2,250 parts per billion. Also assayed for aflatoxin were 21 samples of No. 2 peanuts, part of a 150-sample survey. In laboratory experiments, as much as 475,000 ppb of aflatoxin B_1 has been produced on shelled autoclaved peanuts as the substrate. The aqueous acetone procedure for determination of aflatoxins, originally developed for analysis of cottonseed products, has proved to be applicable to peanuts, and a micro procedure permits determination of aflatoxin in a sample as small as one milligram. Thus aflatoxin content of different parts of a highly contaminated peanut cotyledon ranged from 60,000 to 4,000,000 ppb. This finding of individual peanuts containing large amounts of aflatoxins distributed in different parts of the kernel emphasizes the difficulty of adequate sampling and indicates that simple washing to remove aflatoxin is not feasible. However, it also affords the promise of salvaging the major portion of contaminated lots if a simple method of removing individual contaminated kernels can be devised.

A working standard containing the four aflatoxins, suitable for reference in assaying for aflatoxin by thin-layer chromatography, was prepared and supplied to about 150 laboratories requesting such a standard.

An important part of this research concerns cooperative swine-feeding tests. For the first test, five batches of peanut meals of about 1000 pounds each containing graded levels of 10 to 1400 ppb of aflatoxin B_1, were prepared at SU; swine fed the meals at the University of California at Davis have now been slaughtered, and various histopathological tests are now underway at WU. For the second test, four batches of peanut meal (total weight 8,250 pounds) that contained graded levels of 36 to 5000 ppb of aflatoxin B_1 were prepared at SU. In this case, about 60% of the aflatoxin used was supplied by NU. After the swine-feeding tests are completed at Davis, WU will conduct the requisite biological tests.

In still another phase of the research, three pilot-plant extraction runs were made with peanuts to adapt acetone-hexane-water extraction for simultaneous removal of aflatoxin and oil from peanuts by prepress solvent extraction. Peanut meals containing between 2 and 30 ppb of aflatoxin and less than 1% oil were produced from peanuts containing about 300 ppb aflatoxin. Because of the importance of the aflatoxin problem, cooperation with industry and other government agencies is continuing on a number of projects of mutual interest. (S4-116).

The second related project, being conducted under contract to the Agricultural Experiment Station, Auburn University, concerns the limiting environmental conditions for the elaboration of mycotoxins in peanuts. Preliminary results indicate strain-temperature dependence in the production of

aflatoxin. When autoclaved shelled peanuts having 20% moisture were inoculated into aflatoxin-elaborating strains of Aspergillus flavus, incubation at 25° C. for 7-9 days produced the highest levels of aflatoxin. Production of aflatoxin decreased drastically at 20° C. and at 35-40° C. Aflatoxins were detected in the peanuts after 3 days' incubation and for the 21-day duration of the experiment. In liquid media, one strain of A. flavus produced most aflatoxins at 25° C., whereas another was most active at 30° C. Trace minerals and nitrogen also appeared to be critical. Magnesium and zinc were determined to be essential to aflatoxin synthesis in liquid cultures. Both organic and inorganic nitrogen sources were required for maximum aflatoxin yields. Potassium and ammonium nitrate were found to be the best inorganic sources of nitrogen, while glycine, glutamic and aspartic acids, phenylalanine, tyrosine, and tryptophan were good sources of organic nitrogen in the order named. This finding, with the indication of strain-temperature dependence, suggests that minor differences in the substrate (peanuts) may have profound effects on the elaboration of aflatoxin. Experiments on the influence of a number of variables will make use of the controlled humidity cabinets that were recently installed. (S4 1-121(C)).

The third line of related work is also being conducted under contract, this one to the Agricultural Experiment Station, Texas A&M University. Processing methods used for peanuts of known history will be investigated with respect to different growing and curing conditions to achieve high quality peanut products that are free of mycotoxins. The Starr variety of Spanish-type peanuts were grown with and without irrigation and pre-emergence treatment of the soil with fungicide. Records of rainfall and temperature were kept. Of the threshed portion of the crop, half was artificially dried at 120° F., and the other half, intended for drying at ambient temperatures, had to be partially dried by artificial means because of high humidity. The balance of the crop was field-dried in windrows. Preliminary analyses indicate that irrigation and fumigation improve the quality of raw peanuts, as measured by maturity, density, and crude oil content; in comparison with artificially dried peanuts, field dried lots had a higher percentage of mature kernels, but there was little difference in the crude oil content of these mature kernels. Analyses of raw peanuts will be continued, but the major effort will be on the evaluation of processed products by organoleptic and chemical techniques. (S4 1-120(C)).

B. New and Improved Food Products and Processing Technology

1. Peanut Flours and Derived Products for Human Consumption in Developing Countries. A study of the preparation of peanut flours and their derived products for human consumption in developing countries has been initiated with the support of the Agency for International Development (AID). Investigation of processing in the pilot plant indicated the feasibility of adapting the conventional prepress solvent extraction process to use of a mixed solvent (acetone-hexane-water). This promising method simultaneously extracts the oil, removes about 90-95% of the aflatoxin present, and produces a highly nutritious meal or flour product. Samples of these flours are being

prepared to be evaluated as foods; improvement of quality will permit higher percentages to be incorporated into bakery products and other formulations. Effort will be concentrated on the development of the simplest and most practical processes for small and medium sized plants to produce peanut flours of highest quality. (SU-0-0-3(AID)).

2. New Processed Products, Including Low-Calorie Peanuts and Peanut Flours, Meals, and Grits. A method has been developed for the preparation of low-fat, high-protein peanut products without the use of solvents. The peanuts are mechanically pressed to remove as much as 85% of the oil, expanded to their original size in an aqueous medium, dried, roasted, and salted. Conditions for these steps are being investigated. Two methods of drying and roasting that appear promising are the application of infrared heat to peanuts in a perforated rotating cylinder and immersion in hot oil. The information obtained to date should prove helpful in developing a commercial process. Objectives include improving the texture, appearance, and method of salting, and adapting the process for pilot plant and then commercial production of these attractive, low-calorie peanuts. (S4 1-126).

A contract recently awarded to the Agricultural Experiment Station, Auburn University, concerns the development of peanut products for use in processed and convenience foods. Peanut flours, meals, and grits, some having reduced oil content, will be prepared and from them a variety of foods--such as chips or flakes, milk or malted milk-type drinks, baking flour, ice cream, and other confectionery goods--will be developed and evaluated. Although work is not yet underway, steps have been taken to procure the peanuts and the equipment necessary for this research. (S4 1-118(C)).

3. Methods Developed for Inactivating or Removing Aflatoxin from Contaminated Peanut Kernels. Procedures are being developed to inactivate or remove aflatoxins from contaminated peanut kernels. Treatment with chemicals, especially those based on ammonia, appear to be effective in reducing the aflatoxin content of peanut meals without significantly altering their nutritive value. Anhydrous ammoniation produced good results: peanut meal containing 700 ppb B_1 assayed 17-25 ppb B_1 after being processed at 40 psig pressure at 160-170° F. for one hour. Ammoniation of peanut meats followed by hexane extraction was not as effective. Peanut meal treated with gaseous and aqueous ClO_2 by a cooperating chemical company showed no reduction in aflatoxin, whereas after meal was treated with acid-activated NaOCl (Textone), no aflatoxin B_1 was detectable. Although heat treatments also reduced the aflatoxin content, they may impair the nutritive value. The utility of various treatments will be investigated to develop practical methods of inactivating aflatoxin. Feeding studies will be conducted in cooperation with WU and other groups to better define conditions whereby aflatoxin is destroyed but the nutritive value is not impaired. (S4 1-133, Pending).

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AREA NO. 8 - TUNG PROCESSING AND PRODUCTS

Problem. Tung oil has lost much of its traditional market in protective coatings to synthetic raw materials. New and improved industrial products from tung oil must be developed to recapture lost markets, maintain present markets, and provide new outlets for surplus tung oil. Basic information is needed on the chemical composition and properties of tung oil and its fatty acids, and on the chemical modification of these materials to permit more effective exploitation of their unique characteristics in protective coatings, agricultural and industrial chemicals, surfactants, and plasticizers.

USDA AND COOPERATIVE PROGRAM

Research in the area of chemical composition and physical properties is in progress under a grant of P.L. 480 funds to the National Chemical Laboratory, Poona, India, for investigations of the effect of heat on tung oil and its derivatives, and characterization and identification of compounds resulting from heat treatments, to extend the utilization of tung oil (project duration - 5 yrs.).

The Federal in-house scientific research effort in this area has been terminated. P.L. 480 research involves 1 grant for research on chemical composition and physical properties.

The following line of work was terminated during the year: The development of exterior and interior intumescing, fire-retardant coatings based on tung oil and tung oil derivatives.

PROGRAM OF STATE EXPERIMENT STATIONS

State stations reported no research in this area.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Structural Factors, Properties, and Reactions of the Proteins. The composition, structural factors, properties, and reactions of oilseed proteins and associated materials are being investigated in research conducted by the Seed Protein Pioneering Research Laboratory. The basic information developed should lead to new concepts and possibly new applications for oilseed proteins, including tung protein. Since peanuts were found to be a particularly suitable experimental material and were employed for much of the early pioneering research on seed proteins, the report of progress in this research is given in Area No. 7, "Peanuts Processing and Products," as in the previous report.

2. Basic Investigations of the Effect of Heat on Tung Oil and Its Derivatives. At the National Chemical Laboratory in Poona, India, research to investigate the effect of heat on tung oil and on its derivatives is being conducted under a P. L. 480 grant. Drastic heat treatment of methyl eleostearate afforded low yields of a complex mixture of monomeric materials, shown to contain at least five different monomers. Heating methyl esters of α- and β - eleostearic acids at lower temperatures for longer periods of time gave unexpectedly higher yields of cyclic monomers from the β ester but not from the α ester. Separation yielded two principal monomer fractions to which two alternative structures have been tentatively assigned. Attention is being directed to a study of catalysts and reaction conditions to try to get reproducible yields. The fundamental information generated by this research is expected to aid in the development of new industrial uses for tung oil outside the protective coatings field. (UR-A7-(40)-12).

B. New and Improved Industrial Products

1. Intumescing Fire-Retardant Surface Coatings from Tung Oil Alkyds. Considerable progress has been made in the development of water-resistant, intumescing, fire-retardant coatings based on tung oil and its derivatives, research conducted with the cooperation and support of the U. S. Army Engineer Research and Development Laboratories and the Pan American Tung Research and Development League. Recent experiments have illustrated the importance of a suitable vehicle and of the spumific and carbonific materials. For example, the vehicle synthesized with 33% tung oil appears to be the best type of vehicle for formulating highly water-resistant fire-retardant coatings with pentaerythritol polyurethanes, but the vehicle containing 17% tung oil appears best for formulating fire-retardant coatings with carbonific pentaerythritols. In addition to imparting much more water-resistance, some of these polyurethanes produce coatings having superior color and color retention, good drying and bonding characteristics, and other excellent conventional properties. The development of commercially successful oil-based fire-retardant coatings should not only significantly increase the consumption of tung oil but also greatly reduce losses of life and property.

This progress has been facilitated by modification of the SU 8-foot tunnel furnace to an elementary 16-foot tunnel furnace in which flame-spread can be measured. Since the results correlate well with results from the Underwriters' Laboratories' 25-foot tunnel furnace, only a limited number of coatings have had to be evaluated by costly and time-consuming trials in the longer furnace. A chemical company has duplicated the SU 16-foot furnace for its own use, and a major paint company has requested specifications for construction. (S4 1-113).

New and Improved Industrial Products

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1/ Publication resulting from research supported in part by funds transferred from the U. S. Army Engineer Research and Development Laboratories.

AREA NO. 9 - CITRUS AND SUBTROPICAL FRUITS PROCESSING AND PRODUCTS - SOUTHERN LABORATORY

Problem. The citrus and subtropical fruit production of the Southern Region is an expanding industry with the need for the development of better, as well as new-type consumer products, and for the improvement of present or invention of new processing procedures and machinery. These advances are required to regularly utilize the currently large production, particularly of oranges and grapefruit, and the anticipated higher production of these fruits, to the economic advantage of the growers and consumers. Basic research is needed to lay the groundwork for these advances. This research is needed, for example, on the composition and physical nature of essential oils, flavonoids, including bitter constituents, constituents responsible for oxidized off-flavors, carotenoids, and the like, which determine many of the sensory characteristics, and which affect product quality and stability. Other problems whose solutions are dependent upon the availability of more detailed compositional and physical data are: cloud stability, gelation, discoloration, fermentation, and the like. Increased production of citrus has stimulated the development of new products but many of these are urgently in need of improvement which will depend in part upon advances in basic research. New products are needed to attract new markets and also to reduce packaging and shipping costs. Research is needed to improve frozen citrus concentrates as processing procedures change, to develop better high density concentrate products, citrus powders, chilled juice and section products, pulp-fortified products, and to develop new or improved canned products which have a natural fruit flavor. Research is especially needed on grapefruit to develop practical methods for reducing the bitterness and harshness of juice products and to increase the use of grapefruit juice base in mixed fruit juice blends, drinks, concentrates and the like. Along with progress on product development there is a serious need to improve the actual processing procedures, processing equipment, and packaging operations and materials, to obtain and maintain the most desirable fruit characteristics particularly for citrus powders.

USDA AND COOPERATIVE PROGRAM

The Department has a continuing long-term program involving biochemists, organic chemists, food technologists, and a chemical engineer engaged in both basic and applied utilization research studies on citrus and subtropical fruits of the Southern Region to develop new or extended uses for these commodities.

Research to develop basic information on chemical composition and physical properties of citrus and subtropical fruits, and their products and by-products is conducted at the U. S. Fruit and Vegetable Products Laboratories at Weslaco, Texas and Winter Haven, Florida. This information provides the necessary basis for efficient research in developing new and improved food

products and processing technology. At the Weslaco Laboratory the program includes investigations of the influence of seasonal changes of carotenoid and flavonoid constituents which directly or indirectly affect color and flavor of processed products from Texas colored grapefruit, as a basis for improvement of processing characteristics of and products from these grapefruit. The Texas Agricultural Experiment Station (substation 15, Weslaco), Citrus Rootstock Investigations Laboratory (CR, ARS, Weslaco), the Texas College of Arts and Industries,and Rio Farms, Inc. (Edcouch) are providing grapefruit of known history and conducting, or cooperating in conducting, on-the-tree tests. Additional research on chemical composition and physical properties is carried out under a contract at the University of Oklahoma Research Institute, Norman, Oklahoma, on investigations of the effect of maturity of grapefruit on total flavonoid, naringin, and poncirin; and on the chemistry and nature of naringin and naringin-derived compounds to provide a scientific basis for the control of bitterness in processed grapefruit products. At the Winter Haven Laboratory the program includes: research to identify recently isolated flavones and other neutral orange peel constituents and evaluate their relation to bitterness and harshness in orange products; investigations of the composition of essential oils in citrus products, particularly orange, to provide a basis for improvement in quality and uniformity of citrus products; a study of off-flavor development in processed citrus juice in relation to the lipid composition of the suspended matter; and research to explore means for minimizing or blocking the formation of bitter components in grapefruit, a key step in developing processed grapefruit products of greater attractiveness to the consumer. Close consultation is maintained with the Florida Agricultural Experiment Station (Citrus Experiment Station, Lake Alfred; Citrus Research Investigations (CR, ARS, Orlando); Florida Citrus Mutual (Lakeland); and the citrus processing industry.

Research to develop new and improved food products is carried out at the U. S. Fruit and Vegetable Products Laboratories at Weslaco, Texas, and Winter Haven, Florida. At the Weslaco Laboratory the major applied effort is to develop products which will make greater and more efficient use of grapefruit. This research is being carried out in part in cooperation with several state and private organizations. The cooperators provide fruit or raw materials, such as pulp and juice, of known history. Processing plant facilities are available from the Texsun Citrus Corporation (Weslaco) and Rio-Vac, Inc. (Harlingen). Formal agreements exist with the Texas Agricultural Experiment Station (College Station and Weslaco), with Texsun Citrus Corporation (Weslaco) and with Rio Farms, Inc. (Edcouch). Informal cooperation is maintained with Texas Citrus Mutual, Inc. (Weslaco), Texas Canners Association (Weslaco) and such other organizations as are found necessary for the procurement and processing of fruit. At the Winter Haven Laboratory research is in progress to develop high quality, "instant" citrus powders by new and improved processing technology as described below.

In the field of new and improved processing technology, research is being carried out at the U. S. Fruit and Vegetable Products Laboratory, Winter

Haven, Florida, to determine how the "foam-mat" type of air-drying can be applied for the preparation of dried citrus products of optimum flavor and stability. Foam-mat drying of orange juices, and grapefruit juices, is currently being studied. This research is conducted in cooperation with the Western Utilization Research and Development Division (ARS) and the Florida Citrus Commission under a formal memorandum of understanding. Additional research on new and improved processing technology is being carried out under contract at the Citrus Experiment Station, University of Florida, Lake Alfred, Florida, on the development of a practical and efficient pilot plant scale process for the production of enzymatically debittered grapefruit juice and products with improved flavor, product stability and storage characteristics.

The Federal in-house scientific effort at the Southern Division devoted to research in this area totals 20.6 professional man-years. Of this total 13.2 is devoted to chemical composition and physical properties, and 7.4 to new and improved processing technology. The contract research involves an additional 1.9 man-years, 1.4 being on chemical composition and physical properties, and 0.5 being on new and improved processing technology.

The following lines of work were terminated during the year: (1) Investigation of the chemical and physical nature of components of cloud of orange juice, to provide better understanding and control of factors affecting stability of orange juice products (under Chemical Composition and Physical Properties); and (2) Utilization of natural and debittered grapefruit juice and puree as bases for the development of improved fruit juice blends, drinks, and concentrates (under New and Improved Food Products).

PROGRAM OF STATE EXPERIMENT STATIONS

State stations engage in both basic and applied research on the utilization of citrus and subtropical fruits with the objective of expanding markets and increasing utilization of these crops. Citrus, oranges, grapefruit and tangerines are held in special environmental control chambers and the various combinations of temperature, humidity and airflow are studied to determine subsequent effects on quality. Efforts to reduce decay during storage and transit lead to research on the basic physical, biochemical and physiological changes which occur during handling and marketing. Factors influencing quality of mature avocado fruits are evaluated by study of the respiratory rate, various physiological disturbances, ripening rate and external and internal quality of fruits. Non-destructive physical measurements of quality are sought.

Product research and development includes study of processes for canning grapefruit sections. Special attention is given to problems of texture, structure, flavor and color. The characteristics of commercial frozen Florida orange concentrate and superconcentrate are determined at intervals and used to establish characteristics of these products. Characteristics of canned and frozen concentrated juices are studied initially and after storage

at elevated temperatures. Efforts to extract, separate, identify, and determine quantitatively each of the volatile components responsible for the natural flavors and occasional off-flavors in citrus fruits, citrus oils and processed citrus products continue. The determination of the relationship of all components to the total flavor and aroma presents numerous unsolved problems.

Certain properties of avocado polygalacturonase and papaya pectinesterase are being studied. In addition, the enzymes of the fig latex are being isolated and characterized as to molecular weight, activity and amino acid composition.

Work with subtropical crops such as guava, mango, soursop, banana, pineapple, coffee and plantain involves development of processes for preservation of the delicate and characteristic flavor of these fruits. Production of freeze-dried products of high quality and storage life is under study. Products such as banana puree, fried snack items, fruit powders, candied items, and nectars are receiving attention.

The Hawaii and Puerto Rico stations conduct research to strengthen their coffee industries. These studies include research on the microbiology of the coffee fermentation process, on drying coffee and on the quality and acceptability of the final product. Basic equilibrium moisture content data for parchment and green coffee are being developed to guide design of an experimental system which uses solar energy for drying coffee.

Research designed to recover or make useful products from citrus and pineapple wastes is in progress. Other work is directed to conversion of citrus terpenes to useful chemicals and to use of isolated cultures from natural sources to produce glycerol and glycols from citrus wastes by fermentation. Feasibility studies on the preparation of livestock feeds from farm product and distillery, cannery and brewery wastes continue with materials selected for study being pineapple, citrus and pigeon pea cannery wastes, spent grains and blackstrap molasses.

The research effort devoted to citrus and subtropical fruit utilization research is about 19.6 professional man-years.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Chemical and Physical Properties of Removing Constituents of Florida Citrus and Subtropical Fruit Products. In a new project continuing basic work on the composition of citrus oils to improve the quality of citrus products, nootkatone, an important flavoring constituent of grapefruit, was synthesized from valencene, a major sesquiterpene of orange oil, in a one-step oxidation using t-butylchromate. This accomplishment provides an additional source for nootkatone as a flavoring material.

Rapid analysis of hydrocarbons by use of the Time-of-Flight Mass Spectrometer has facilitated identification of the constituents of the essential oils in citrus products. The process, which offers semiquantitative analysis, can be completed in about 90 minutes and requires only 1-2 ml. of oil. Thirteen citrus oils investigated include processed oil, juice oil, condensate oil, and oils of orange (several varieties), grapefruit, tangerine, lemon, and lime. Fifteen sesquiterpenes including α- and Δ-elemene have been identified in citrus oils. A high concentration of valencene, the principal constituent in orange juice oil, was found in grapefruit juice oil. The procedure for isolating alcohols from citrus oils was simplified. Nineteen alcohols have been found in orange cold-pressed oils, 10 of which had not been previously reported in orange oil--in fact, four of these 10 had never been reported in any natural product. Seventeen alcohols in grapefruit oil have been identified as c- and t-linalool oxide, linalool, actanol, c- and t-2,8-p-menthadiene-1-ol, nonanol, α-terpineol, decanol, citronellol, geraniol, c- and t-carveol, undecanol, dodecanol, elemol, and 8-p-menthene-1,2-diol. Composition studies will continue to include other oxygenated materials in the oil. (S3 2-48).

2. Investigation of the Bitter Principle and Flavonoids in Citrus Products. In another new project that continues work already begun, the monitoring study of peel juices for the 1963-64 season has been completed; combined with the 1962-63 results, it provides information on variation in peel juice bitterness for a normal season and for one in which a freeze occurred. Much of the bitterness resides in the neutral fraction of the benzene extract, an analysis of which has accounted for 80% of the constituents. The structure of the unknown flavone in the neutral fraction of orange peel juice extract was identified: it is tetramethoxy scutellarein (5,6,7,4'tetramethoxy-flavone). Although this compound has been synthesized and prepared as a derivative of related flavones, it has never before been found in natural products. A recently developed method of analysis by thin-layer chromatography has permitted determination of flavones constituting 60 to 90% of seven neutral fractions of peel juice extract. Their ranges are: tangeretin, 2.1-14.8%; tetra-O-methylscutellarein, 6.1-10.3%; heptamethoxyflavone, 7.6-11.0%; nobiletin, 20.6-26.0; and sinensetin, 19.2-28.2%. A new compound was also detected, and efforts to isolate it are being continued. The analytical data suggest that there is a correlation between tangeretin content and bitterness, but taste tests have not yet verified that this is the most important bitter constituent. Preliminary results utilizing a method of analysis developed by Australian scientists suggest that some bitter Florida orange concentrates contain limonin, which is a lactone and therefore not expected to occur in a neutral fraction and never before demonstrated in Florida orange juice. However, if tangeretin and limonin do prove to be important bitter principles, they can be estimated, respectively, by the new methods of analysis developed by Division and Australian scientists.(S3 2-47).

Significant progress has been made by the contractor (University of Oklahoma Research Institute) in determining the effect of grapefruit maturity on total flavonoids and on naringin and poncirin. A second naringin (naringin 2) that may be the nonbitter naringenin 7-rutinoside has been isolated. In midseason

juice, the ratio of naringin 1 (bitter) to naringin 2 (possibly nonbitter) was 3 to 1; in late-season juice, this ratio was 2 to 1. Total naringin value of late season juice was approximately 75% that of midseason juice, the decrease being almost entirely in the amount of naringin 1. If it can be demonstrated conclusively that naringin in grapefruit may exist in both bitter and nonbitter forms and that the former decreases as the season progresses, the basic knowledge will be provided to aid in identifying factors affecting bitterness and to improve quality control in processing of grapefruit. A recently developed chromatographic-fluorometric method for the determination of naringin, naringenin rutinoside, and related flavone glycosides in grapefruit juice permits more accurate assay of bitterness. Approximate R_f values for the various compounds separated on thin-layer chromatographic plates were: isosakuranetin rutinoside, 0.67; poncirin, 0.60; hesperidin, 0.50; neohesperidin, 0.43; naringenin rutinoside, 0.37; and naringin, 0.30. The chromatographic-fluorometric method affords a tool for following the degree of bitterness as it is affected by maturity, breeding, and environmental factors, and also provides the basis for developing simpler methods of processing control. Before the contract terminates, the flavonoids of Texas Red Grapefruit harvested at monthly intervals will be differentiated. (S3 2-39(C)(Rev.)).

During the related investigation on bitterness and harshness in Florida grapefruit products, nine coumarins were isolated from grapefruit: four were identified as coumarins previously reported in grapefruit; three as coumarins not previously reported in grapefruit; and the remaining two have not been completely identified, although one was classified as a coumarin and the other as a psoralen. None of the coumarins tasted are bitter. Research on bitterness of grapefruit is continuing under a new project, S3 2-49. (S3 2-42).

The new project on bitterness in grapefruit products is directed toward minimizing the biogenesis of bitter constituents through enzymatic inhibition, thus obviating the need for removing them by expensive processing. The use of radioisotopes will afford a technique selective enough to explore particular metabolic pathways to the exclusion of others, and sensitive enough to detect and identify minute quantities of compounds. The first step will be to establish the immediate precursors to naringin and poncirin. For grapefruit, this step will be investigated by use of radioisotopically labeled acetate and cinnamic acid, shown in other plants to be precursors to the C-15 nucleus of flavonoids. To date, only nonradioactive materials have been used, while steps preparatory to use of radioactive materials have been taken. Since several required radioactive compounds are not commercially available, synthetic procedures applicable to radiosyntheses were investigated with nonradioactive compounds. Thin-layer chromatography and electrophoresis were explored as means of isolating and identifying compounds related to bitterness. A highly purified sample of naringin was prepared and a standard ultraviolet absorption curve constructed to be used in the quantitative determination of bitterness. (S3 2-49).

3. Factors Affecting the Physical Characteristics of Processed Citrus Products. Analyses of the cloud of orange juice are now complete and the project has been discontinued. Juice was sampled from the three major varieties of oranges, and the study included early and midseason ranges, representative of normal and freezing seasons. In addition, the composition of albedo, rag, pulp, and juice from two samples of Valencia oranges was compared with cloud components recovered by centrifugation from commercially extracted juices. Neither fruit variety nor freeze damage to fruit on the tree produces major differences in the composition of cloud in orange juice. Also, excessive maceration of structural tissue during extraction and finishing does not contribute materially to cloud; nor does avoidance of this practice reduce cloud. The previously reported theory that natural cloud comes from the juice rather than from mechanical disintegration of structural tissue was thus confirmed: there was a high lipid content of fine cloud recovered by centrifugation, and high levels of nitrogen and phosphorus in the solvent-insoluble fractions of fine cloud, whereas there were low amounts of these constituents in albedo, rag, and pulp.

A method for more accurate, precise, and rapid determination of recoverable oil in citrus juices was developed. The complete determination requires only 25 ml of juice and 10 minutes, in contrast to 2 liters of sample and about one and a half hours for the official method. All variable conditions of the method have been studied, there remaining only its application to samples from the full range of commercial citrus varieties. Since recoverable oil content is an important factor in quality grading of citrus juice products, this method should gain acceptance in industry: the Florida Canners' Association has recommended that it be brought to the attention of the Institute of Food Technologists. (S3 2-38(Rev.)).

4. Basic Investigations of Carotenoids in Grapefruit. Verification of the biochemical mechanisms involved in the biosynthesis of carotenoids in colored grapefruit and other fruits and vegetables would facilitate improvement of processing. In recent investigations of the relationship of carotenoids to color, flavor, and processing reactions, tomatoes were used as a model system because they synthesize carotenoids much more rapidly than do grapefruit. To determine the concentration of carotenoids at different stages of maturity, spring and fall Homestead tomatoes were analyzed according to the standards listed in Tomato Color Classification, USDA, 1961. Of the carotenoid pigments determined, only alpha- and beta-carotene were found in the mature green stage; these two, as well as zeta- and gamma-carotene, phytofluene, and lycopene, were found in the breaker stage; phytoene was not found until the turning stage. Since the concentrations of these carotenes decrease or increase during different stages of maturity, it may be possible to use their ratios as a measure of maturity of tomatoes. Also of importance is the evidence that the concentration of pro-vitamin A is highest in the light red stage of maturity. This work supports the theory that different carotenes are made via different metabolic pathways. In addition to providing information on the general problems of carotenogenesis, this study on the concentration and ratios of carotenes should prove useful to breeders of Homestead

tomatoes in selecting lines capable of maximum color development and to processors as a precise measure of maturity. In another phase of this work, an extract of parsley was prepared to isolate and identify the nonsaponifiable material that has chromatographic properties similar to the carotenes. Eleven different compounds were found by thin-layer chromatography, whereas over 20 compounds were found in a sample sent out for analysis by gas chromatography. Additional work will be conducted with respect to nonsaponifiable material. Preliminary work, to be expanded under a new project, has shown that the carotene content of grapefruit treated with paraffinic oil sprays is higher than that in unsprayed fruit. This type of treatment may offer a way to augment the carotene and lycopene in grapefruit and to delay loss of color during the harvest season. (S3 2-34(Rev.)).

B. New and Improved Food Products

1. Development of New Grapefruit Based Beverages. Good progress has been made in the investigation of the flavonoids in Texas grapefruit, the control of bitterness in grapefruit products, and the development of debittered grapefruit juice that can be used in processed products. Those advances, together with related research in other Federal laboratories, offer promise of imminent development of successful beverages. Radio-carbon studies have confirmed the hypothesis that flavonoids develop primarily during early growth of the grapefruit. Fruit harvested from trees exposed at monthly intervals, beginning with the period of spring bloom, to carbon dioxide tagged with carbon-14 were analyzed for the tagged flavonoids to determine the sequence and time of their development in the maturing fruit. Full-grown fruit from trees treated in November 1963 had no detectable activity in the flavonoids. Prunin is one of the flavonones found to be present in young fruit. Continuing work on the tagged fruit, coupled with the fluorometric analysis of flavonoids recently developed under another project (S3 2-39(C) (Rev.)) should provide valuable information on the accumulation and modification of bitterness during the season and its effect on the processed product. New analytical methods that have aided in the study of the flavonoid bitterness of grapefruit include a simple method for extracting flavonoids from citrus juice and a chromatographic solvent system for excellent separation of flavonoids.

Additional work has been done on debittering grapefruit juice by enzymatic treatment or by resins. Enzymatic hydrolysis with naringinase C-100 of flavonoids present in grapefruit showed the enzyme to be nonspecific; consequently, use of this enzyme may have an undetermined influence on juice quality. Since some of the polyamide resins used in the other type of debittering process irreversibly absorb some of the minor flavonoids, their repeated use may be limited.

Several formulations have been developed for concentrated fruit juice punches in which natural or partially debittered grapefruit juice is the major juice constituent. Tasters rated punches prepared from half-debittered grapefruit juice preferable to those prepared from normal juice or from completely

debittered juice. Punches flavored with raspberry or strawberry were judged best and warrant consumer acceptance studies. (S3 2-40).

C. New and Improved Processing Technology

1. Application of Foam-Mat Drying to Citrus. In cooperation with WU and the Florida Citrus Commission, the research to improve the storage stability and quality of foam-mat citrus powders is continuing. Reconstitution has been improved by vacuum packing, repackaging in CO_2, or packing under CO_2 positive pressure. Such packing obviates reconstitution difficulties previously associated with use of monoglyceride foaming agents. A good foaming procedure has been developed for the recently installed Oakes mixer, and the new crater dryer can now be used to routinely produce orange and grapefruit powders having lower moisture content achieved at lower temperatures. The foaming procedure has now been modified so that less than 0.5% additive on a solids basis is required. Freeze-dried orange and grapefruit powders have been prepared for use as flavor additives, and their use could make foam-mat powders equivalent in quality to frozen concentrates. Orange powders have been stored at 60° F. or lower for over 39 weeks without detectable change in flavor. A compound that was chromatographically separated from off-flavor powders but not from control powders or concentrate has been isolated and identified as 5-hydroxymethylfurfural; a routine method of testing for its presence shows promise as a quality control process. Two machinery companies and many food and packaging companies have expressed interest in this process and in plans for consumer testing. Plans include continued study of the relation of time and temperature of drying to product quality and to storage characteristics, a continued investigation of the use of freeze-dried powders, and organoleptic evaluation of various combinations of foam-mat and freeze-dried powders. (S3 2-43).

Under other cooperative research with WU and the Florida Citrus Commission, foam-mat dried grapefruit powders having commercially acceptable storage stability have been developed. At 70° F. or less, they would last for eight months to a year without detectable changes and for much longer before consumer acceptance would be seriously reduced. Either cans or plastic-laminated foil pouches could be used for commercial distribution. Improved foaming procedures permit drying on the crater dryer to less than 1% moisture content and enable preparation of very satisfactory foam by use of Methocel alone in concentrations of less than 0.5% total additive on a solids basis. Drying at lower temperatures and reduction in amount of additive enhances the fresh-juice quality of reconstituted powders. Consumer acceptance tests are being planned in cooperation with the Florida Citrus Commission, technical assistance has been given to one company using an adaptation of the foam-mat process, and many food and packaging companies have expressed interest in the process and in the plans for testing consumer acceptance. (S3 2-41).

2. Process for Enzymatically Debittering Grapefruit Products. A new contract has been negotiated with the Florida Agricultural Experiment Station to develop a practical and efficient pilot-plant process for the production

of debittered grapefruit juice and grapefruit products by means of commercially available enzymes. The project is designed to improve palatability and acceptance, increase stability and quality retention during storage, and provide engineering and cost data applicable to commercial production. The preliminary experiments have been designed, the processing equipment readied, and a planning conference held to formulate a work schedule. However, difficulty experienced in obtaining a pound of commercial naringinase enzyme obviated its use for pilot plant studies on early (bitter) grapefruit and has necessitated postponement of work until a new crop of grapefruit becomes available in October 1965. In the meantime, cans of commercial grapefruit sections were shown to vary widely in naringin content. In a series of analyses to determine how rapidly equilibrium diffusion occurs in canned grapefruit sections, naringin values during storage as long as three weeks did not increase over the initial analysis made six hours after canning. A new laboratory finisher which does not apply pressure to the pulp during extraction is being secured for use in the research; the effect of this new principle of extraction will be investigated. (S3 2-46(C)).

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AREA NO. 10 - VEGETABLES PROCESSING AND PRODUCTS - SOUTHERN LABORATORY

Problem. Although extensive progress has been made in recent years in developing stable, attractive, and convenient to use vegetable products, new and improved processed products must be developed and means of stabilizing perishable vegetables provided to minimize the adverse effects of seasonable surpluses and unfavorable markets, and to provide an adequate supply of good food for a growing population. Product quality needs to be improved and processing cost reduced through the adaptation and application of the latest technological developments and nutritional findings. For example, a major problem of the cucumber industry, since most of the crop is brine-cured, is to improve the curing process so that no loss occurs in the value of the cucumber during the brine-curing and storage process and the cost of processing is reduced. New pure culture fermented products are needed to more fully utilize cucumbers and many other vegetables in attractive consumer items. As another example, a precooked, dehydrated, sweetpotato product has been developed which usually has good shelf life when sealed under an inert gas. It reconstitutes to a product having the characteristics of freshly cooked and pureed sweetpotatoes. Applied research on a pilot-plant scale is needed to obtain additional engineering and processing data applicable to commercial production of flakes from sweetpotatoes of different variety and environmental history. Basic research is needed to further improve quality and storageability of the product, and to provide the scientific basis for the development of a process for making excellent flakes from uncured, freshly dug sweetpotatoes. There is a continuing need in the use of vegetables for processing to investigate the characteristics of the raw material as these characteristics are affected by climate, soil, cultural practices, breeding and the like. Celery, already an important flavoring ingredient, could become much more important if the factors and constituents responsible for the intensity, variableness, and stability of its flavor could be controlled in processing, and processed products of improved flavor and convenience could be developed. Many vegetables grown in the Southern Region differ in their chemical and physical characteristics from the same crops grown in the more temperate regions. Tomatoes are a good example in that they are frequently poorer in color, flavor and texture. Several vegetable crops, including sweetpotatoes, hot peppers, okra, and Southern peas, are grown almost exclusively in the Southern Region. More utilization research is needed to complement the Federal and State production research programs and to provide cooperation in the form of composition and processing studies. This kind of cooperation is needed to prevent the release of breeding selections which are entirely unsuited for processing.

USDA AND COOPERATIVE PROGRAM

The Department has a continuing long-term program involving biochemists, organic chemists, microbiologists, food technologists, and chemical engineers

engaged in both basic and applied utilization research studies on vegetables of the Southern Region to develop new or extended uses for these commodities.

Research to develop basic information on chemical composition and physical properties of vegetables, their products and byproducts, is conducted as a basis for efficient research in developing new and improved food products and processing technology. Investigations of the flavor and aroma components in natural and pure culture fermented cucumber pickle products are carried out at the U. S. Food Fermentation Laboratory, Raleigh, North Carolina, to provide the basis for producing pickle products of greater consumer acceptability. The North Carolina and Michigan Agricultural Experiment Stations, and the Pickle Packers International, Inc., cooperate in this research. Other research at Raleigh, conducted at and in cooperation with the North Carolina Agricultural Experiment Station, is concerned with basic investigations of the chemistry and biochemistry of the carotenoid pigments in vegetables in relation to variety, maturity, and environmental factors, to facilitate the development of improved and more attractive processed products. Additional research on chemical composition and physical properties is being carried out under a grant at the Research Triangle Institute, Durham, North Carolina, on elucidation of the molecular structure and chemical characteristics of the pectinase inhibitor in sericea forage and other plant sources which has proven effective in preventing softening of cucumbers in brine curing.

In the field of new and improved food products by processing of vegetables, both basic and applied research are being carried out at New Orleans, Louisiana, to improve the stability of the flavor of precooked, dehydrated sweetpotato flakes packaged in air, and to improve the processability of uncured sweetpotatoes and their flake characteristics. These are two major problems still facing the new sweetpotato flake industry. Current research approaches involve evaluation of antioxidants and other additives for flavor stabilization, and investigation of commercial amylolytic enzymes in accelerating the curing of sweetpotatoes. Basic studies of the properties of native amylolytic enzymes of the sweetpotato are included. Close cooperation is maintained with the Louisiana Agricultural Experiment Station, and industry and industry associations. Research is in progress at the U. S. Fruit and Vegetable Products Laboratory, Winter Haven, Florida, on the development of processed celery products of improved flavor and convenience. Research is also being conducted at the U. S. Fruit and Vegetable Products Laboratory, Weslaco, Texas, to develop new and improved processed products from southern grown vegetables other than sweetpotatoes and celery. The Texas Agricultural Experiment Station and industry associations provide raw materials of known history for this research.

Research on new and improved processing technology is conducted at New Orleans, Louisiana, and at the U. S. Food Fermentation Laboratory, Raleigh, North Carolina. Pilot-plant investigations are being carried out at New Orleans to develop new and improved processing methods applicable to commercial manufacture of stable, precooked, dehydrated sweetpotato flakes

from sweetpotatoes of different varieties and environmental history. Processing variables currently being investigated include the effect of variety, curing, type of cooking, drying conditions, and various food additives. Cooperation is maintained with the Marketing Economics Division, ERS, for the market evaluation of improved flake products, and with the Louisiana Agricultural Experiment Station, the Louisiana Sweetpotato Association, the Louisiana Sweetpotato Commission, and various industrial concerns. At Raleigh the objective of the research is to improve pickle processing technology and the quality of the products. Current emphasis is on investigations of methods for the controlled fermentation of cucumbers and other vegetables by application of pure culture techniques to fermentation practices in order to reduce processing costs and improve product characteristics. Limited cooperative work is conducted to evaluate new cucumber varieties (or selections) for processing into brine-cured and fresh-pack products. Cooperation is maintained with the North Carolina Agricultural Experiment Station. The Michigan State University (Department of Microbiology) is also cooperating by providing technical assistance in the controlled fermentation studies. The Pickle Packers International, Inc. contributes support to the research and supplies raw material.

The Federal in-house scientific effort at the Southern Division devoted to research in this area totals 22.1 professional man-years. Of this total 4.5 is devoted to chemical composition and physical properties, 12.1 to new and improved food products, and 5.5 to new and improved processing technology. The domestic grant research involves an additional 0.9 man-year, on chemical composition and physical properties.

PROGRAM OF STATE EXPERIMENT STATIONS

State stations conduct a broad program of basic and applied research on vegetable processing and products in order to maintain the place of vegetables in the diet and to overcome problems associated with the perishability and seasonality of vegetable crops. Research on the adaptability and evaluation of vegetable varieties for processing is a continuing service to vegetable breeding programs. Each promising introduction or variety is evaluated with respect to processing yield and characteristics.

Increased public concern with protection of the food supply from pesticide residues has resulted in initiation of three regional projects to study reduction or removal of residues from food products. Since commercial food processing and preparation procedures vary, the effect of these processes on residue removal is being evaluated. There is also an urgent need to develop rapid, sensitive methods for routine determination of pesticide residues on foods undergoing commercial processing. Data relative to chemical form, distribution and persistence is being amassed. Vegetables are included in the crops being studied. One objective of regional project NEM-30 involves study of the basic physiology and chemistry of changes taking place in post-harvest handling and processing.

Characterization of raw materials extends to consideration of the effects of various production variables upon processed product quality. Mechanical harvesting and the associated effects upon ultimate processed product quality are receiving increasing study. The degree of correlation or association between color, flavor and texture in fresh and in processed items continues to be a major concern.

Basic chemical and physical properties of vegetables are related to product acceptance and quality. Research on vegetables in this area ranges from standard composition studies to highly specialized analysis for mineral components. Research aimed at describing the biological changes that occur in vegetables at different stages of maturity continues. The role of enzymes and pigments in vegetables also receives continuing study.

Basic microbiological research centers around the high resistance of bacterial spores to heat and the adverse effects extreme thermal process requirements have on canned vegetables. Microbiological studies extend from determination of thermal process requirements to study of the natural flora of fresh vegetables. The radioresistance of bacterial spores and use of combined antibiotics and heat are carefully researched.

Processing technology research is directed to studies of freeze-drying, brining, canning, fermentation, hydro-cooling and controlled atmosphere methods. The comprehensive study of the effects of controlled or modified atmosphere on the biochemical, physical and quality characteristics of various vegetables continues.

New or improved product development research seeks to improve or perfect such items as "quick cooking" peas and beans, beet chips, various snack items; soups; and new sauerkraut products. Basic information relative to composition, nutritive value and functional properties are emphasized.

The total station research effort devoted to vegetables processing and products is 64.1 professional man-years.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Compositions and Physical Properties

1. Identification and Characterization of Flavor and Aroma Components of Pickle Products. A basic study conducted in cooperation with the Pickle Packers International, Inc., and the North Carolina and Michigan Agricultural Experiment Stations has shown much promise in revealing the necessary blends of chemical constituents responsible for both desirable and undesirable organoleptic reactions to fermented pickle flavor. The volatile components have been determined from the pure culture fermentation of brined cucumbers produced by cultures representing four species of lactic acid bacteria (Lactobacillus plantarum, L. brevis, Pedicoccus cerevisiae, and Leuconostoc mesenteroides). Uninoculated natural and pasteurized controls were also

analyzed.

The following six compounds were identified from the pure culture fermentations: formaldehyde, acetaldehyde, propionaldehyde, acetone, butyraldehyde, and ethyl alcohol. Two additional compounds were obtained from the natural fermentation (control), namely, ethyl butyrate and isovaleraldehyde. Perhaps the most important contribution of the work to date has been the demonstration that gas chromatography is a useful tool in the study of pure culture vegetable fermentations. Differences in vapor chromatograms were obtained both between species of lactic acid bacteria and between strains of the same species, a finding of vital importance in selecting the most desirable organism for fermentation purposes. The results further indicated that the flavor of fermented pickles is the result of a blend of volatile components rather than the presence or absence of a single component.

Variations in the taste of the vinegar used in the manufacture of commercial pickle products can readily influence their flavor. Research on the volatile components of different vinegars showed marked differences in the number and kinds of components of three natural (cider, wine, and tarragon) and two distilled vinegars. Of 22 different volatile components identified by gas chromatography, 5 were present in all the vinegars and most of the others were present in the natural vinegars, whereas they were strikingly absent from the two distilled vinegars, which had, respectively, only 6 and 11 of these compounds. (S3 5-21).

2. Identification and Characterization of Inhibitor of Enzyme That Softens Cucumbers. Related research being conducted under a new grant to the Research Triangle Institute stems from the observation by Division scientists that the enzyme pectinase, which adversely softens commercial brine-cured cucumbers, can be inhibited by a water extract of muscadine grape leaves (Vitis rotundifolia) or of the forage crop sericea (Lespedeza cuneata). The work is directed toward elucidating the molecular structure and chemical characteristics of this pectinase inhibitor in sericea forage and in other plant sources, the initial step being purification of the active principle from sericea and grape leaves. (S3 5-24(Gr.)).

3. Investigations of the Chemistry and Biochemistry of the Carotenoid Pigments in Vegetables. In cooperation with the North Carolina Agricultural Experiment Station, the chemistry of the carotenoid pigments in vegetables and fruits is being studied in relation to variety, maturity, and environmental factors. The project is founded partially on results of previous investigation of carotenogenesis in grapefruit. The finding that a carotene, contained in a carotene protein complex, stimulates the photo-reduction of ascorbate in the presence of DPN is believed to be the most direct evidence of a function of carotenoids in plant tissue yet found. This protein complex contains carotene hydrocarbons, mono-, and polyhydroxy carotenoids; the relative abundance of carotene hydrocarbons is significantly less than in the intact leaf. Since mixtures of carotenes appear to be inhibitory if the concentration is too high and thus crude preparations are very

concentration-sensitive, progress toward identification has been limited so far to indirect approaches. However, active fractions of a polyhydroxy carotene that is not nearly so concentration-sensitive have recently been obtained. From partition behavior, the active compound appears to be a dihydroxy carotene. An attempt will be made to identify the individual carotenes contributing to the stimulation of the photosynthetic reaction; a mutant tomato high in β-carotene will be fractionated and its precursors compared with those in the red tomato; and an attempt will be made to identify the carotene precursor previously isolated from high lycopene tomatoes. (S3 5-28).

B. New and Improved Food Products

1. New and Improved Dehydrated Sweetpotato Products. Continued work to develop stable sweetpotato flakes from different varieties of sweetpotatoes has revealed that flakes made from apparently comparable, high quality sweetpotatoes in different crop years may differ markedly in shelf-life. In contrast to previous observations, when flakes in an atmosphere of nitrogen containing less than 2% oxygen remained stable for a year or longer, similar flakes made from cured Goldrush sweetpotatoes during 1963-64 had a shelf-life of only three to four months. However, flakes made from the latter lots of roots with the addition of butylated hydroxyanisole, butylated hydroxytoluene, and citric acid were still stable at 10 months. Other research indicates that a good flake product can be made from sweetpotatoes immediately after harvesting by use of any one of three equally effective commercial enzyme preparations. Antioxidant-synergists prolong the shelf-life of these flakes to about the same extent as flakes made from cured roots, but the BHT-BHA-citric acid is still the best known additive for this purpose; no substitute has been found for packaging the flakes in an inert atmosphere. Analytical, viscometric, and enzymatic susceptibility tests indicate that starch changes are not the variable primarily responsible for process or storage differences.

An important result is the discovery of a new amylolytic enzyme having unique properties: its high activity at 65 to 78°C. but low activity at temperatures below 45°C. is highly significant, compared with commonly known amylases. At high temperatures, it has great activity at pH 5.8-6.3 but loses all activity at pH 7.0 and above. Freshly harvested sweetpotatoes contain little of this enzyme, curing does not increase it, but storage at 60°F. results in a progressive rise. This discovery could lead to improved methods of curing sweetpotatoes and also for processing uncured sweetpotatoes, as well as making a significant contribution to enzyme chemistry. (S3 5-25).

2. Development of Processed Celery Products of Improved Flavor and Convenience. Puffed dried celery with commercial possibilities has been developed, and work is continuing to improve its properties, particularly with respect to flavor fortification. Pretreating celery with a calcium chloride solution before blanching or rapid freezing in liquid nitrogen, which eliminates blanching, both promise to improve the texture of the rehydrated product. Color, though primarily dependent on the fresh material, can perhaps be

improved by refinements in drying conditions. More uniform slicing will permit more uniform drying and puffing and therefore improve appearance and rehydration. Development of off-flavor is also being investigated, preliminary results indicating a quantitative difference between the headspace vapors of samples stored at temperatures of -90°, 0°, 40°, and 10°F. Rectification of condensate from steam-distilled celery has been attempted to obtain and concentrate celery flavors. Results from a new larger and longer column show marked improvement in fold and percent recovery. However, more work is necessary to delineate the optimum operating parameters. Processing of 1,400 lbs. of field-run celery showed that 25-30% is left fallow as waste, over half of which shows good potential as a flavor source since it yields almost twice as much flavoring material as the more edible portion of the stalk. The remaining field waste would be of interest for puff dried celery. Among procedures to be attempted in recovering flavoring materials from high-fold essences include adding ethanol either prior to rectification or to the essence after rectification and then freezing the aqueous ethanol solution to remove the water, or using solvent pairs of varying miscibility. Possible changes in relative composition at each stage of recovery will be followed. A revised project will cover phases of the work to be investigated in the near future. (S3 5-23).

3. Development of New and Improved Processed Products from Texas Vegetables. Research is continuing in cooperation with the Texas Agricultural Experiment Station to improve food products processed from southern-grown vegetables, including carrots and tomatoes. Carrot flakes stored for 15 months in an atmosphere of nitrogen have remained the same in ascorbic acid but have decreased slightly in carotene content. Taste tests indicate that flakes packaged in nitrogen and stored at -5°F. may be preferred to those stored at 68°F. Peeling and firming tomatoes in one operation should aid in canning whole tomatoes. The skin of the tomato is ruptured during the blanching operation in a hot, highly concentrated solution of calcium chloride and can be removed by jets of water. Investigations at a canning plant have demonstrated that Chico, LaBonita, Homestead, and M-66 varieties can be thus treated. These four varieties (M-66 added this season) are also being evaluated for the effect of their pectic substances on the consistency of canned juice. Studies of the seasonal variations in Chico tomatoes showed that percent acid and total solids decreased from first harvest (June 17) to last harvest (July 16), whereas pH and Brix remained approximately the same. A major problem is contamination of the calcium chloride peeling solution with tomato pulp; continuing replacement would make the process prohibitively expensive. A lesser problem is the need to find uses for the "tailover" juice made from brokens, pieces, and skins of tomatoes that had passed through the calcium chloride process; its experimental use to cover the calcium-firmed tomatoes when they were canned made them too rubbery and increased the amount of calcium above that permitted by U. S. Standards. Evaluation of new vegetable varieties will continue under this cooperative research. (S3 5-22).

C. New and Improved Processing Technology

1. Development of Processing Methods Applicable to Commercial Production of Dehydrated Sweetpotato Products. Continuing success of sweetpotato flakes is implicit in the interest currently shown by industry. One plant went into commercial production for the 1964-65 season, another expects to be in production this season, and a large food processor is rapidly assembling equipment to make trial runs. Technical assistance has been given to three existing plants, one new plant, and seven prospective plants, and three additional states have requested information. At the same time, research to extend and improve the process is continuing. The effects of drying variables on the rate of drying and on flake quality have been established and made available to the commercial plants.

Further tests of Georgia Red variety sweetpotatoes with additives such as salt, corn syrup, monosodium glutamate, amylolytic enzymes, and various combinations of these agents have not yet produced passable reconstituted flakes, although salt reduced the inherent sour flavor. The light color of these flakes is accounted for by analyses revealing only half as much beta-carotene in Georgia Red as in Goldrush, without color preservatives, the reconstituted flakes and puree discolor rapidly. Flakes prepared this season had a much better taste than those from the 1963-64 crop. Various processing variables have been investigated and a complete material balance conducted on the processing of this variety.

The processing of uncured Goldrush sweetpotatoes has been studied with respect to use of various sugars and use of enzymes. A method of processing uncured sweetpotatoes by utilizing the natural enzymes present in the sweetpotato has been found to produce flakes comparable in quality to those produced by adding commercially prepared enzymes. Optimum conditions of time and temperature have been established. Studies on the Centennial variety have begun, and processing will be extended to include Jersey Orange, Red Velvet, and Julian. (S3 5-25).

2. Investigations to Improve Quality and Reduce Cost of Processed Cucumber and Other Vegetable Products. The groundwork has been laid for the development of a new kind of vegetable fermentation product. A pure culture fermentation process has been described for the controlled fermentation of brined cucumbers. Although many problems must be solved before commercialization of the process, adaptation of a commercial culture medium for the isolation and growth of the fastidious lactic acid bacteria should open the way for the development of improved control and processing methods and for their application in vegetable and other lactic acid fermentation processes. The pure culture fermentation process, developed for cucumbers with the cooperation of the North Carolina and Michigan Agricultural Experiment Stations and Pickle Packers International, Inc., is now being evaluated for use with other vegetables. The pure culture fermentation of green tomatoes, cherry peppers, carrots, and a mixture of these vegetables with cucumbers was the first time this had been done. Pure culture pickles from the four-vegetable mixture were rated as "Good" for overall acceptability; although evaluation of the individual vegetables has not yet been completed, the process appears to offer the

same advantages for them as for cucumbers. Routine testing is also in progress on 100 pure culture fermentations of Spanish-type green olives in brine, into which one of four species or several species mixtures of lactic acid bacteria were inoculated. In addition, 28 lots of pure culture dill pickles evaluated after five months' storage were also rated "Good" by a technical panel composed of pickle plant operators and by a consumer panel. Pickles from naturally fermented controls were rated "Not acceptable." Throughout the past four years, 26 lots of pure culture dill pickles evaluated by 38 consumer panels in several states all rated "Good." Essentially the same evaluation was obtained for pickles inoculated with single species of lactic acid, such as L. plantarum and Ped. cerevisiae, or with a mixture of the two species.

The leaves of sericea forage (Lespedeza cuneata Don) or a freeze-dried extract prepared from it can prevent softening of cucumbers in the presence of pectinolytic and cellulolytic enzymes, an illustration that naturally occurring plant enzyme inhibitors from this or other sources may have application in the fermentation industry. A large amount of fresh sericea has been prepared and sent out for extraction of the purified enzyme inhibitor to be used in further testing. (S3 5-27).

Because of the seasonal nature of the work, during this reporting period there has been no activity in the evaluation of new cucumber lines and varieties for commercial pickling. However, it is anticipated that assistance and supervision will continue to be provided to breeders and pickle packers in cooperation with the North Carolina and Michigan Agricultural Experiment Stations and Pickle Packers International, Inc. (S3 5-22).

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

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AREA NO. 11 - NAVAL STORES PROCESSING AND PRODUCTS

Problem. More uses for pine gum, rosin and turpentine need to be developed through research to provide industrial markets for current and anticipated production of gum naval stores. Recent decreases in uses of gum rosin, especially in paper size, has resulted in the accumulation of a considerable surplus of this commodity. Other types of rosin as well as synthetic chemicals backed by strong industrial research programs have made serious inroads on the traditional markets for gum rosin. Gum turpentine is also faced with similar competition. If the turpentine farmers of the southeast are to continue to find profitable markets for their pine gum, existing knowledge of the properties of this commodity and its derived products must be used to develop new uses and strengthen old ones. New fundamental information about the chemistry of the terpenes and resin acids is also needed to fully exploit their unique characteristics. New or expanded uses for naval stores products are especially needed in polymers, plastics, elastomers, resins, plasticizers, surface coatings, textile finishes, odorants, insecticides, herbicides, and other large-volume industrial chemicals. There is also a serious need to improve existing processes and develop new processing technology for the industry.

USDA AND COOPERATIVE PROGRAM

The Department has a continuing long-term program at Olustee, Florida, involving organic chemists and a chemical engineer engaged in both basic and applied research to discover and develop new and improved uses for pine gum and its products. In research to develop new and improved industrial products from pine gum, rosin, turpentine, or their components, conversion of the resin acids derived from gum rosin and pine gum to new polyfunctional products by reaction with suitable chemicals is under investigation to develop intermediates for production of resins, plastics, and related products. Another research approach involves the condensation of the unsaturated (olefinic) materials present in pine gum with certain reactive chemicals (dienophiles) to produce industrially useful chemicals. Research is being conducted to develop improved polyester resins from resin acids of pine gum and rosin; to study the preparation and reactions of epoxides and ozonization products of resin acids and their derivatives to produce materials having potential for use in plastics and other industrial products; to develop practical methods for converting levopimaric acid, resin acid mixtures, and/or pine gum to polyfunctional compounds useful in plastics, resins, and other industrial products by formaldehyde addition and subsequent reactions; to convert terpene acids, terpene acid derivatives, and rosin derivatives into polymerizable monomers suitable for making new polymers, plastics, and resins; and to produce reactive chemical intermediates from turpentine and terpenes derived from it by reaction with inexpensive dienophiles. The Pulp Chemicals Association has been supporting a Fellowship at the Naval Stores Laboratory for the purpose of conducting research to develop a suitable

method for determining rosin and rosin derivatives in protective coatings, a necessity if rosin is to be allowed in certain types of these coatings from which it is now excluded. This research has been successfully completed. Informal cooperation is maintained with other agencies and industrial firms in connection with the naval stores research program. The U. S. Forest Service cooperates by supplying selected samples of pine gum.

Additional research on new and improved industrial products is in progress under contract at the University of Cincinnati, Cincinnati, Ohio, on the application of the oxo and related reactions to terpenes and resin acids to produce new, useful alcohols, aldehydes, and/or acids, and the characterization of the products thus obtained; at Cornell University, Ithaca, New York, on the synthesis of terpene alcohols and glycols for use in the production of new and useful terpene derived polymers; and at the University of Florida, Gainesville, Florida, on the development of a practical process for the conversion of α-pinene to dimers in good yields, and the conversion of these dimers to useful, reactive derivatives.

Research in the field of chemical composition and physical properties is in progress under a grant of P.L. 480 funds to the Juan de la Cierva School of Technical Investigations, Barcelona, Spain, for development of new or improved methods of preparing selected terpene alcohols for use as standards, to obtain basic information on the composition and properties of products made from pine gum (project duration - 3 yrs.)

The Federal in-house scientific research effort in this area totals 15.0 professional man-years. All of this effort is on new and improved industrial products. The contract research involves an additional 2.7 man-years on new and improved industrial products. P.L. 480 research involves 1 grant for research in the field of chemical composition and physical properties.

The following lines of work under new and improved industrial products were terminated during the year: (1) Preparation of chemical intermediates from pine gum products for use in the preparation of new synthetic polymers, plastics and resins to expand the utilization of turpentine and rosin; (2) Hypochlorite modification of rosin and resin acids for use as chemical intermediate for preparation of new industrial resins, surface coatings, plastics, rosin soap emulsifiers and similar materials; (3) The utilization of photosensitized oxidized pine gum and components in the fields of plastics and rubber.

PROGRAM OF STATE EXPERIMENT STATIONS

State stations did not report work in this area.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Composition and Physical Properties of Pine Gum. Contract research at Purdue Research Foundation is developing fundamental information on the chemical transformations of terpene olefinic compounds by hydroboration and subsequent reactions. A systematic examination of the stereochemistry of the hydroboration reaction products of Δ 3-carene has been undertaken. In research thus far on the hydroboration of d-limonene, it has been found that selective external hydroboration can be achieved by reacting this terpene with disiamylborane (di-s-isoamylborane) at room temperature. In situ protonolysis studies have shown that the resulting organoborane can be quantitatively converted to 1-p-menthene (carvomenthene) by reacting with dry isobutyric acid. The research findings should ultimately provide the basis for the synthesis of potentially useful products from terpenes. (S4 1-112(C)).

B. New and Improved Industrial Products

1. Development of Intermediates for the Production of Resins, Plastics, Plasticizers, and Other Industrial Products from Pine Gum and its Components. A study of the chemistry of the epoxides of esters of α-campholenol has been completed. The epoxides react in a manner such that their use in epoxy resins appears very unlikely. Their reaction with organic acids produces a mixture of compounds. The major component is a diol formed as a result of molecular rearrangement, and the other compound produced is a keto alcohol, which could be considered the normal reaction product. The diacetate of the mixture has attracted interest of perfume chemists. Copper chromite reduction of diethyl sym-homopinate gave almost quantitative yield of a cis and trans mixture of sym-homopinane diol (2,2-dimethyl-1,3-(2-hydroxyethyl)cyclobutane). This symmetrical glycol has unusual thermal stability and should be very useful industrially. (S5 2-38).

Research is being conducted to prepare polymerizable monomers for vinyl and condensation-type polymers from terpene and resin acid derivatives. Linear alkanoic and alkenoic esters of α-campholenyl epoxides were found to be acceptable primary plasticizers for polyvinyl chloride, imparting excellent long-term thermal stability to the plastic compositions. Since cheap fatty acids can be used to prepare these esters they should have industrial potential. α-Campholene aldehyde and diethyl pinate have potential as perfumes and are being evaluated by industry. Procedures have also been developed for preparing interesting glycols from pinonic, pinolic and homopinic acids, and presumably from pinonaldehyde. It is planned to place more research emphasis on rosin rather than terpene acids. The preparation of vinyl ethers of abietol and β-hydroxyethyl abietol and the vinyl ester of 6-hydroxymethyltetrahydroabietic acid will be studied. Research on the synthesis of a number of polyethylene glycol esters and ethers of rosin-derived di- and tricarboxylic acids and alcohols will also be initiated. (S5 2-55).

In further studies of the reaction of terpenes with dienophiles to produce useful chemical intermediates, three compounds were isolated from the reaction of fumaric acid with α-terpinene. Two of these were characterized as

normal 1:1 adducts; the other is an unexpected, abnormal adduct. The production of the latter compound may be of considerable theoretical importance and may also affect the utility of the products. Dimethyl fumarate adds to α-terpinene to give the three corresponding methyl esters. Exploratory experiments have shown that dimethylmaleate adds readily to α-terpinene, gamma-terpinene, terpinolene and β-pinene, but not to α-pinene, dipentene or 2,4(8) p-menthadiene, to give 1:1 adducts. Even at 300° in the absence of acid the various terpenes do not isomerize and give the same adduct, and they differ widely in the ease with which they form adducts. These various reactions will be studied further. (S5 2-48).

In research to develop practical methods for preparing the levopimaric acid-formaldehyde adduct and selected derived products for industrial uses, yields of 80% of crystalline adduct have been obtained from 90% pure levopimaric acid using a solvent system which is applicable to large scale runs. The reaction can be run to give complete reaction of the levopimaric acid but in this case part of the adduct is converted to 6-methylolabietic acid. Also, 50% yields of crystalline adduct have been obtained directly from pine gum by procedures which can be scaled up without difficulty. Hydrogenation of the double bonds of the 6-methylolabietic acid gives a saturated hydroxy acid which is not susceptible to air oxidation. Reductive procedures are being investigated for converting the adduct to the potentially useful glycol product. (S5 2-51).

The research on hypochlorite modification of rosin and resin acids to produce chemical intermediates for industrial products has been discontinued. It was found that both abietic and levopimaric acids react readily with sodium hypohalite to introduce hydroxyl groups into the resin acid molecule. By this reaction, 6-hydroxyabietic acid was produced in 50% conversion from pure levopimaric acid with isolation of 30% of the purified material. Such a hydroxylated resin acid, or hydroxylated rosin, should be of value as a low cost extender for polyester and polyurethane resins. (S5 2-44).

Contract research has been initiated at the University of Florida on the development of a practical process for the conversion of α-pinene to dimers in good yields, and the conversion of these dimers to useful, reactive derivatives. All three catalysts investigated thus far for the dimerization reaction (boron trifluoride, phosphoric acid and sulfuric acid) produced complex products which contained isomerized terpenes, trimers, and polymers along with the desired dimers. The relatively good yields of mixed dimers (in excess of 60%) obtained at this early stage of the work is encouraging. Efforts will be made to improve the techniques for separating and identifying the products and to find conditions which give less complex mixtures. (S5 2-49(C)).

2. Addition of Chemicals to Rosin Acids With Emphasis on Photochemical Methods to Produce Chemicals Useful in Manufacturing Surface Active Agents, Textiles, Paper and Plastics. In further research on photosensitized-oxidized pine gum (POPG), this material was converted to a mixture of diepoxides, from

which the lead, barium and other metal salts were prepared. The lead and barium salts proved to be effective as stabilizers for poly-(vinyl chloride). The barium salt of POPG itself was an effective stabilizer and also exhibited antimicrobial activity. Industry has expressed interest in these products; they should provide a new, potential large-scale use for POPG other than as a low-cost source of free radicals. Another product prepared in the research--the hydroperoxide of methyl dihydroabietate--also has aroused the interest of industry. Some exploratory work on the strong-base isomerization of some major resin acids of gum rosin was carried out. Potassium tertiary-butoxide in dimethyl sulfoxide isomerized levopimaric acid to abietic acid. This is the first base-catalyzed isomerization of a resin acid that has been accomplished. In other work, gum rosin was maleated and varying portions of the anhydride carboxyls were neutralized with base. Under conditions simulating tank car storage, the samples treated with base did not crystallize as did the blank. On preparation of paper size from these materials, the same good results were obtained. A noncrystallizing fortified paper size should be of immediate interest to certain paper size manufacturers. This project has been discontinued and promising research leads on the preparation and reaction of diepoxides from photosentized-oxidized rosin and resin acids are being investigated under a new project. (S5 2-47).

3. Conversion of Rosin Acids, Pine Gum and Turpentine into New Polymers, Protective Coatings, Resins and Plastics. Research has been initiated on the preparation and reactions of epoxides and ozonization products of resin acids and their derivatives to produce materials having potential for use in plastics and other industrial products. An improved process for preparing mixed diepoxides from photosensitized-oxidized pine gum (POPG) was developed. There is considerable industrial interest in POPG and the mixed diepoxide product. Crystalline products--12-α-hydroxyabietic acid and presumed 8α, 12α-dihydroxy-Δ^{13}-abietic acid--were isolated in good yield from the reaction of levopimaric acid with peracid. It should be possible to obtain polyhydroxy compounds of potential use in manufacturing polyurethane foams from resin acids in this manner. In exploratory work on the strong-base isomerization of some major resin acids of gum rosin, the isomerization of levopimaric, palustric, and abietic acids was accomplished with potassium tert.-butoxide in dimethyl sulfoxide to give an equilibrium mixture of about 70% abietic acid, 5% neoabietic acid, 5% palustric and/or levopimaric acid, 5% of a new resin acid, 5% of a second new resin acid, and 10% of dehydroabietic acid in all cases. The preparation of polyamide-polyimide plastics, a new class of heat-resistant plastics, from maleopimaric acid and diamines was attempted but the desired high polymers have not yet been obtained. The chemistry of resin acid epoxides will be explored in an effort to find industrially useful derivatives. (S5 2-52).

Research has been initiated to develop improved polyester resins from resin acids of pine gum and rosin. Polyesters prepared from glycol and glycerol esters of heat polymerized rosin by further reaction with fumaric acid and diethylene glycol show promise. Cured ester-styrene copolymers of these

polyesters equivalent to the better commercial products were obtained. Studies of methods for converting rosin acids into dibasic acids have shown that moderate yields of dibasic acids can be obtained by reaction of rosin with permaleic acid. The dihydro acids present in disproportionated rosin also react in a similar manner. The dibasic acids obtained in this way should be useful in a variety of products such as polyesters, polyamides and paper size. A practical method was discovered for isolating dehydroabietic acid from commercial disproportionated rosin in good yields and excellent purity. It involves recrystallization of the ethanol amine salt of the disproportionated rosin from aqueous alcohol. This should encourage the commercialization of some of the derivatives of this acid. Also, the practical, less expensive method developed for preparing metal resinates directly from pine gum or from a mineral spirit solution of rosin should lead to increased utilization of these resinates. (S5 2-53).

The experimental work on polymerization of pine gum derivatives carried out under contract at the University of Arizona has been completed. Recent work has involved studies of the polymerization of vinyl butyl amidecarbonylcyclobutane acetate with vinyl chloride, and of selected terpenes with ethylene and propylene. An evaluation sample of the copolymer of the aforementioned acetate with vinyl chloride (75% by weight) was prepared by using GRR soap (sodium laurate) as an emulsifier. Repeated precipitations from tetrahydrofuran gave white polymers, inherent viscosity 1.23, that on dissolving in the solvent gave colorless solutions. Conditions have been established for the production of terpolymers of ethylene-propylene-dipentene with varying amounts of unsaturation using Ziegler-type catalyst systems. Unsaturation in terms of grams of polymer containing one mole equivalent double bond ranged from 2720 to 67, inherent viscosities from 0.598 to 1.54, and softening range from 110-130 to 150-180° C. Samples of the terpolymers are being evaluated for vulcanizability. They may have industrial potential for this or other crosslinking reactions. Copolymers of vinyl chloride with vinyl 2,2-dimethyl-3-morpholineamidecyclobutane acetate, vinyl 2,2-dimethyl-3-di-n-butylamineamidecyclobutane acetate, and vinyl 2,2-dimethyl-3-piperidineamidecyclobutane acetate were prepared, purified, and their physical properties determined. (S4 1-89(C)).

Contract research at U. S. Industrial Chemicals Corporation has been initiated on the free-radical high-pressure copolymerization of ethylene with selected unsaturated gum naval stores compounds to produce industrially useful products. Conditions have been established for the free-radical high-pressure copolymerization of ethylene with α-pinene, dipentene, 3,7-dimethyl-1,6-octadiene, myrcene, alloöcimene, and mixed resin acids. Maximum concentrations of these monomers for stable reaction were found to be 21, 12, 21, 14, 4, and 11%, respectively. Products containing 3% and 10% of the monomers were also prepared, where feasible, for evaluation. Reactions of monomers having less unsaturation were easier to control and produced more interesting looking products. Although the products were of too low molecular weight for blown film, some of them may offer promise for less conventional plastics applications. (S4 1-115(C)).

Research on the application of the oxo and related reactions to terpenes and resin acids to produce alcohols, aldehydes, and acids has continued under contract at the University of Cincinnati. Optimum conditions have been worked out for hydroformylation of dipentene to produce a monounsaturated aldehyde in moderate yields (about 50%). It will be possible to use the aldehyde as such or to convert it to an alcohol, acid or amine by known methods. Attempts to produce difunctional derivatives by further hydroformylation of the aldehyde or by direct addition of formaldehyde to dipentene were unsuccessful. Abietic acid did not hydroformylate under normal conditions due to abnormal behavior with cobalt carbonyls. Further efforts will be made to obtain difunctional derivatives. (S5 2-45(C)).

Further contract research on the synthesis of terpene alcohols and glycols by reaction of selected terpenes (camphene, limonene, and α-pinene) with formaldehyde has been conducted at Cornell University. Good yields of 8-hydroxymethyl-camphene and its acetate have been obtained. Product yield and purity depend on the reaction conditions. With stannic chloride as the catalyst the major reaction product of camphene with formaldehyde is a hydroxymethyltricyclene; with boron trifluoride it is a meta-dioxane. The major condensation product of formaldehyde with limonene has been identified as 10-hydroxymethyl-limonene. Yields and purity of this alcohol or its acetate have been improved but are still lower than with camphene. Alpha-pinene gives a complex mixture of products when either mild or strong acid catalysts are employed. The major alcohols prepared in this research will be evaluated from the standpoint of their conversion to esters and ethers, particularly polymeric or polymerizable ones. (S5 2-46(C)).

The cooperative research with the Pulp Chemicals Association to develop a method for the determination of rosin and rosin derivatives in protective coatings has been completed. The method of analysis developed under this project should permit the use of small amounts of rosin in many formulations from which it was previously excluded. (S5 2-39(Rev.)).

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New and Improved Processing Technology

Wells, J. A., Halbrook, N. J., Lawrence, R. V., and O'Connor, R. T. 1965. Intensity of the C≡N stretching vibration in cyanoethylene adducts of levopimaric acid. Appl. Spectry. 19, pp. 26-28.

AREA NO. 12 - PROCESSING AND PRODUCTS - SUGARCANE

Problem. Quotas established by the Sugar Act effectively prevent the accumulation of surpluses by limiting production to estimated requirements at stable, and normally low prices for sugar. Prices received by farmers of the United States and Puerto Rico for sugarcane are based upon the recoverable sugar content of the cane; and the rising costs of production and processing make imperative the more efficient recovery of increased amounts of sugar to provide adequate returns for both processors and growers. Currently recovery of 75% of the total sugar in the cane is considered satisfactory in Louisiana, and about 83% in Puerto Rico and Hawaii. Improved processing methods could increase the recoverable sugar to at least 85% in Louisiana and over 90% in other areas. The development of more efficient processing methods depends in turn upon the acquisition of adequate data on the quantitative composition of juices extracted from sugarcane, and of materials processed to recover sugar. The chemical industry provides a promising potential for the utilization of additional sugar since more than 40 billion pounds of chemical products are produced annually and sold to every section of American industry. More information is needed on the chemistry and properties of products from sugar to expand their utilization and on the application of these derivatives in the production of plastics, protective coatings, emulsifiers, detergents and the like.

USDA AND COOPERATIVE PROGRAM

Research on chemical composition and properties is being carried out under a grant of P.L. 480 funds to Kyoto University, Kyoto, Japan, for isolation and identification of the nucleic acid derivatives of cane molasses, in order to obtain information applicable to expanding the utilization of molasses industrially and in feeds (project duration - 2 yrs.).

The Federal in-house scientific research effort in this area has been terminated. P.L. 480 research involves 1 grant for research on chemical composition and physical properties.

The following line of work was terminated during the year: (1) Investigation of extractable complex polysaccharides of sugarcane in relation to efficiency of recovery and purification of sugar. (2) Pilot plant development of improved methods of purification of juices and sirups to increase sugar recovery and reduce costs of processing sugarcane. (3) Chemical and physical investigations of sugar refining operations to improve processing of cane sugar.

PROGRAM OF STATE EXPERIMENT STATIONS

Station sugarcane utilization research begins with studies directed to obtaining new, early maturing or cold-tolerant varieties which have a high

yield and are adaptable to standard milling procedures and extends to work directed to preparation of flavored syrups for food use.

Most of the basic and exploratory research is carried out at the Puerto Rico station. Use of ion-exchange procedures for the production of sugars that may be utilized without further purification is under continuing study. Other work in progress involves: development of pilot-plant fermentation procedures for fermenting molasses mashes to produce rum; development of distillation procedures for high efficiency rum distillation; search for new strains of yeast for use in fermentation of blackstrap molasses and other materials derived from sugarcane; and determination of factors affecting the sucrose content of cane.

The study which was carried out in cooperation with USDA and which pertained to utilization of sorgo juice for sirup and sugar production is being terminated.

Indiana station research seeks to synthesize analogues of important metabolic sugars wherein hetero atoms such as sulfur, selenium or nitrogen replace the normal oxygen atom. Sugar analogues and their derivatives will be tested for usefulness as medicines or as agricultural chemicals.

The research effort on utilization of sugarcane is 4.9 professional man-years.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Basic Studies of the Chemical Composition and Physical Properties of Sugarcane Juice and Its Products. Knowledge of the composition of the characteristic soluble polysaccharide constituents ("gums") of sugarcane may provide a basis for developing methods to determine the concentrations present in juices, sirups, and raw sugars.

Experiments have continued on freshly harvested, hand-cleaned cane from which levorotatory polysaccharide was previously isolated. Crusher juice expressed without addition of water, and maceration juice obtained from the residue by further extraction with water in two successive crushings, were treated separately with alcohol to precipitate the crude gums. These preparations yielded 8 g. having a specific rotation of -42°, and 13 g. having a specific rotation of -44°, respectively, of the levorotatory polysaccharide, essentially identical with that obtained previously from crusher juice only, which had a specific rotation of -43°. Analyses showed that this polysaccharide was composed of high percentages of pentoses and relatively little glucose, a distribution which indicates that the material is virtually free of contamination by adventitious dextrans. This reproducibility of the isolation of the levorotatory polysaccharide from uncontaminated cane establishes its importance as a natural constituent of juices. Optimum conditions

for complete hydrolysis of the polysaccharides and minimum destruction of sugar are 20 to 25 minutes in 4N hydrochloric acid at 100° C. Analyses of the hydrolyzed polysaccharide showed the following composition: glucose, 2.73%; fructose, 1.3%; galactose, 15.4%; rhamnose, 3.0%; arabinose, 30.0%; and xylose, about one-half the concentration of arabinose. The galactose and rhamnose content of molasses polysaccharide, which is contaminated with dextran, is much lower than that of fresh juice polysaccharide. This relationship suggests that the amount of natural polysaccharide in the total nondialyzable polysaccharides could be estimated by determination of the galactose in the hydrolyzed total polysaccharide.

The phenol-sulfuric acid method, which gives higher color yields than anthrone for colorimetric determination of pentoses, was used to analyze the purified gums. The procedure requiring dialysis of samples for determination of total gums was too cumbersome for routine use, and a simpler method was devised for application in factory control laboratories and in cooperative work with the Crops Research Division at Houma.

Analyses of amylose-amylopectin ratios and starch content of juice samples collected during the 1964 season have been completed. The data indicate that sugarcane starch composition (amylose/amylopectin) is affected by the plant's growth rate and variety. Therefore, the method employed for analysis of total starch should be one that gives quantitative results which are independent of variations in starch composition. (S5 1-81).

In a two-year project being conducted at Kyoto University in Japan under a P. L. 480 grant now nearing termination, an investigation is underway to isolate and identify the nucleic acid derivatives that occur in sugarcane molasses. Thin-layer chromatography, ion exchange chromatography, and continuous liquid-liquid extraction are being used to isolate the nucleic acid derivatives. The separation of bases and nucleosides, an important biochemical problem, was attempted by gas-liquid chromatography, but so far has been unsuccessful. However, a technique involving trimethylsilylation was found to afford easily distillable derivatives. By this technique followed by quantitative hydrolysis with aqueous alcohols, 18 bases and nucleosides were separated amd identified. In the course of the work, a new component was found and its presence confirmed. The structure of this component is being investigated. The basic information obtained in the project is expected to be useful in assessing the role of minor non-sugar components in sugarcane processing and in the use of cane molasses for feed and industrial applications. (UR-A11-(50)-7).

2. Investigations of the Fundamental Chemistry and Physics of Sugar Refining. In cooperation with the Cane Sugar Refining Research Project, Incorporated, an association of commercial sugar refiners, basic investigations of the chemistry and physics of sugar refining were conducted to improve processing of sugar. The molecular weights of gums isolated from juices and molasses were found to be larger than the maximum value, about 500,000, amenable to determination by osmometry; this result agrees with the

previous estimate from light scattering measurements that the weight-average molecular weights range from 700,000 to 3,000,000.

The reducing sugars in molasses, long regarded as a simple glucose-fructose mixture termed "invert," have been shown to consist of more complex mixtures, including mannose and psicose. It is imperative to know the quantitative composition of this major portion of molasses solids, since it affects the amount of sugar that can be crystallized. Reproducible estimates of the amounts of glucose, fructose, and mannose in the reducing fractions were obtained for samples of refinery and raw factory molasses. Total reducing sugars ranged from 9.2 percent in one refinery sample to 22.1 percent in one factory sample; mannose ranged from 0.14 to 3.13 percent of the weight of the molasses. Glucose ranged from 37.7 to 50.6 percent of total reducing sugars. There was wide variation in the individual sugars and total reducing sugars expressed as percentage of the total molasses and of individual sugars expressed as percentage of total reducing sugars. Analysis of an additional refinery molasses sample provided evidence of a nonreducing, levorotatory constituent other than the known sugars in the fraction separated by chromatography on carbon columns.

The chemistry of the precipitation of basic calcium phosphates in water and in aqueous sugar solutions was also investigated. An understanding of the precipitation of this material is essential, for it is used in clarification, the least understood step of the refining process. By crystallography of the basic calcium phosphates in clarifier scums, the principal precipitate was identified as octacalcium phosphate, though anhydrous dicalcium phosphate and hydroxyapatite are also present. The effect of various solution parameters and foreign ions on the crystal habits of the basic calcium phosphates was studied by means of the petrographic microscope.

In an attempt to separate sugar colorants, high voltage paper electrophoresis was not successful in separating the colors of molasses. About ten fractions that were not always sharp have been demonstrated by fluorescence and various reagent sprays. However, the color remains spread over the entire region with little separation. (S5 1-77).

B. New and Improved Processing Technology

1. Processing Procedures to Improve the Refining Quality of Raw Sugar. As selectively bred canes produce higher yields, removal of tops and trash by present harvesting machines becomes less effective. The effect of additional impurities introduced into the juice by grinding this material was investigated in cooperation with the American Sugar Cane League to anticipate problems in clarification and provide a basis for attempting to modify the process to overcome these problems. Pilot-plant clarification tests of topped and new canes from the 1964 crop were completed essentially as planned. To determine the effect of cane tops on clarification, control canes were cut by hand at the top and bottom without the leaves being stripped from the stalk, whereas test canes were harvested in the same manner except that the

tops were left on 50% of the stalks to simulate cane harvested mechanically from badly lodged fields. Trash content on stubble cane harvested early in the season averaged 10% and 3%, respectively, on test and control canes. In comparison with the controls, test canes had twice the amount of soil in juice, required 30 percent more lime, and produced 15 percent more clarifier mud; their clarified juice was 20 percent lower in clarity, 3.5 points lower in purity, 20 percent higher in CaO, and 35 percent higher in P_2O_5.

New canes evaluated were: 1) the most recently released commercial cane, C.P. 55-30; 2) the new standard commercial variety, C.P. 52-68; and 3) one unreleased variety, L. 60-1, the latter of which was harvested by machine and burned during adverse weather and hence is not directly comparable to the first two samples. Operations and average clarifier juice quality factors for the two commercial varieties were essentially identical, except that C.P. 55-30 produced less clarifier mud. The results on pot-liming, limited to a few tests, were not encouraging, since it requires additional clarifier capacity.

Methods developed in the pilot plant to improve the refining quality of raw sugar offer potentially valuable information to processors and refiners. The largest sugar refinery in the area was assisted in evaluating the rapid Millipore membrane-type test to determine the filterability of melted raws. One of the refinery filters is being operated under controlled conditions to correlate data from this test with operating data. If the test proves reliable, this independent evaluation by a refiner should expedite its acceptance by industry.

In addition, the need for better harvesting machines to remove higher percentages of cane tops and trash was well demonstrated and should stimulate efforts to develop improved equipment. (S5 1-80).

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Chemical Composition and Physical Properties

Friloux, J. J., Cashen, N. A., and Cangemi, S. J. 1965. The effect of freeze damage on some of the nonsugar constituents of sugarcane. Sugar y Azucar 60(1), pp. 43-46.

New and Improved Processing Technology

Coll, E. E., Guilbeau, W. F., Jackson, J. T., and Cangemi, S. J. 1964. Juice clarification experiments on two commercial flocculants--1963 Louisiana crop. Sugar Bull. 42, pp. 314-317.

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Guilbeau, W. F., Jackson, J. T., Coll, E. E., and Cangemi, S. J. 1964. Sugarcane processing polyelectrolytes in juice improve mud filtration.

Sugar Bull. 43, pp. 38-40.
Smith, B. A., Sanchez-Nieva, F., Gonzalez, M. A., and Matos-Maldonado, M. 1964. A comparison of several noninverting ion-exchange systems used in the purification of Puerto Rican sugarcane juices. J. Agro. Univ. Puerto Rico 48, pp. 247-254.

AREA NO. 13 - REPLACEMENT CROPS - UTILIZATION POTENTIAL

Problem. Farmers could achieve more economic use of their land if new and profitable crops were available for their choice that would have different end-use patterns from those presently grown. For example, it would be advantageous to develop a new oilseed crop yielding unique fatty acids that could find industrial use in applications for which acids from presently available domestic oilseed crops are unsuitable. To develop a new crop, three basic steps are involved: (1) Survey of wild plants, in cooperation with plant scientists, to identify those having both potentially valuable components and promising agronomic potential for use in the U. S.; (2) detailed physical and chemical characterization of components of interest to obtain clues to likely end uses; (3) selection of the most promising species followed by additional utilization research to explore uses and demonstrate industrial potential and by additional agronomic research to establish proper cultural practices and select the best strains and varieties. Only after these steps have been successfully accomplished can a proposed new crop be offered to agriculture and industry for introduction and development. Obviously, a program of this type is a long-range one. Yet, whether the future of agriculture involves conditions of surplus, of greater emphasis on foods and feeds, or of necessity for greater national self-sufficiency, the nation will benefit from availability of optimum, practical crop plants to serve its needs.

To achieve the objective, survey and characterization work needs to be greatly increased, since the greater the number of species examined, the greater will be the opportunities for finding plants meeting the criteria of high utilization and agronomic potential. Work of the Department has already revealed several promising sources of new potentially valuable water-soluble gums, pulp fibers, and oils containing unique fatty acids such as hydroxy unsaturated acids, capric acid, epoxidized acids and unusual long-chain fatty acids. In order to demonstrate the potential of these new materials, further work is required on their physical and chemical properties and reactions, on processing to obtain maximum recovery from source plants and on by-products from processing, such as oilseed meals.

USDA AND COOPERATIVE PROGRAM

The Department has a continuing long-term program involving an organic chemist engaged at the U. S. Fruit and Vegetable Products Laboratory, Weslaco, Texas, in research to determine the chemical characteristics of juices obtained from selected new varieties of sweet sorghum canes grown in the Rio Grande Valley of Texas, and the effects of cultural and harvesting practices on the chemical characteristics in relation to suitability for sugar recovery; close cooperation is maintained with Substation 15, Texas Agricultural Experiment Station, Weslaco, Texas for growing and harvesting the seeds provided by the Crops Research Division.

The Federal scientific effort at the Southern Division devoted to research in this area totals 1.3 professional man-years. All of this effort is on chemical composition and physical properties.

The following line of work was terminated during the year: Preparation of chemically modified fatty acids or oils, from the potential new oilseed crops Cuphea, Limnanthes, and members of the Umbelliferae, suitable for evaluation as corrosion inhibitors, biologically active compounds, in plastics, or other industrial products.

PROGRAM OF STATE EXPERIMENT STATIONS

Discovery and preservation of valuable plant germ plasm is a continuing objective of the station program in new crops. Much of the research in this area is being done via four regional projects and in cooperation with regional centers. A large portion of the work is cooperative with USDA. Each year many plant introductions are grown and evaluated. Annual and perennial crops possessing potential for industrial or agricultural use are further evaluated for agronomic and chemical qualities. These include crops for paper pulp, pigments, drugs, tannins, essential oils, insecticides, polysaccharide gums, and oils rich in acids of unusual structure. Assay of native and introduced tropical plants for products of economic value receives special attention. New varieties of fruits, vegetables, and grasses better resistant to disease and drought are continually sought.

Basic aspects of this program involve study of the biochemical and physiological basis for difference in crop plants. Attempts are made to determine if differences in biochemical or physiological processes can be associated with particular factors related to quality. Information concerning carbohydrate transformations is sought through study of carbohydrate formation and enzyme mechanisms. Horticultural specialty crops are gaining in importance. A number of studies are underway to facilitate rapid development of this industry.

The total scientific effort devoted to replacement crops is 8.4 professional man-years.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Investigations of Chemical Characteristics of Sweet Sorghum to Evaluate Its Potential for Recovery of Sugar. Since sweet sorghum is needed as a replacement for crops subject to freeze and as an aid to the Rio Grande Valley's overall economic stability, investigations of the chemical characteristics of new sweet sorghum canes have been initiated to determine whether it is possible to grow and process them for sugar. Field tests were designed to evaluate variety, time of planting, and soil requirements. Most of the 430 samples of juice pressed from sweet sorghum from the 1964 date-of-

planting field tests have been analyzed for Brix, pol, and apparent purity to permit agronomic evaluation of the cane varieties and to determine the length of the season during which they can be grown to produce satisfactory quantities of sugar. Analyses of many of these materials for their true dry solid and invert sugar contents have also been made as a basis for calculating juice impurities such as starch, organic acids, and minerals. However, many of these data require checking for three to five seasons before reliable estimates and recommendations can be made about variables that influence a specific variety's potential production of sugar. (S5 5-51).

B. Industrial Utilization

1. Industrial Products from Oilseeds Containing Capric Acid or Unusual Long-Chain Unsaturated Acids. In the research on new oilseed crops, work was completed on the preparation of chemically modified fatty acids or oils to be evaluated for use as industrial materials.

Uses for Cuphea llavea oil, whose major constituent is capric acid, were sought. The oil was extracted from seed for evaluation in the preparation of alkyd resins and as a plasticizer for polyvinyl chloride. Though unsuitable as a primary plasticizer, Cuphea oil improved the low temperature properties of polyvinyl chloride when used as a secondary plasticizer in conjunction with dioctyl phthalate (DOP). Derivatives of capric acid were also submitted for testing as antimicrobial agents and as growth regulators to retard the flowering of tung trees.

Essentially pure methyl 5-eicosenoate and pure methyl 5,13-docosadienoate and their acids were prepared from Limnanthes mixed methyl esters. The former acid was used in the preparation of derivatives for evaluation. One-hundred-gram quantities of the vinyl esters of chlorinated 5-eicosenoic acid and chlorinated Limnanthes mixed fatty acids were prepared for evaluation as copolymers for vinyl chloride. A hydroxy delta-lactone prepared from 5-eicosenoic acid may be a versatile intermediate in the preparation of other materials. A sample of Limnanthes douglasii seed grown in Alaska and analyzed for oil, moisture, nitrogen, and fatty acid composition of the oil was similar to seed grown elsewhere. The predominant acid present in the oil was 5-eicosenoic.

The vinyl ester of the adduct of petroselinic acid (a major acid of Umbelliferae seed oil) and hexachlorocyclopentadiene, prepared under this project, was shown under contract research at the University of Arizona to have utility as a copolymer for vinyl chloride. Four substituted amidostearic acids were prepared from petroselinic acid and submitted for screening as antimicrobial agents. Other nitrogen-containing derivatives of petroselinic acid were sent to a major company for evaluation as corrosion inhibitors. A sample of fennel seed, grown in Texas, was analyzed for moisture, oil, total nitrogen, and fatty acid composition, and found to be similar to samples of fennel seed from other areas. (S5 5-52).

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Industrial Utilization

Novak, A. F. and Fisher, Mary J. (LSU, Baton Rouge, La.); Fore, Sara P. and Dupuy, H. P. (SURDD). 1964. Antimycotic activity of some fatty acid derivatives. J. Am. Oil Chemists' Soc. 41, pp. 503-505.

AREA NO. 14 - RICE PROCESSING AND PRODUCTS

Problem. The productive capacity of U. S. rice growers has increased faster than domestic and export consumption over the past decade, thus limiting the income potentially available from this major world food grain. Detailed knowledge of chemical composition and physical properties, as related to processing is needed to guide milling, processing and product development of U. S. rices so that they can better meet the quality and new product requirements needed for expanded markets. New and diverse food products from rice that are easy to prepare, have flavor and texture appeal, and are economical to manufacture, are needed to increase the total consumption of rice both domestically and abroad. Additional needs include the development of improved milling machinery and techniques, primarily to increase the yield of head rice; intensified research on deep milling to evaluate and utilize the products, protein flour and residual kernels; and research to provide greater flexibility in the industry by developing from either medium or long grain rice new products that will provide on cooking either discrete kernels or a gelatinous food.

USDA AND COOPERATIVE PROGRAM

The Department has a continuing long-term program involving at New Orleans, Louisiana, biochemists and analytical chemists engaged in basic and exploratory studies on the distribution of the chemical constituents of milled rice in consecutive layers of the kernel with special emphasis on nutritionally important constituents such as proteins, amino acids, starch, lipids, vitamins and minerals; and on the cooking and chemical characteristics of the kernels remaining after differential removal of these layers. Findings from this research will provide the necessary basis for evaluating the economic feasibility of using high-protein rice flours (layers removed by deep milling) for protein fortification of foods and as dietetic or other specialty type foods.

Close cooperation is maintained, under formal memoranda of understanding, with the Louisiana, Arkansas and Texas Rice Experiment Stations, who supply rice samples of known variety and cultural history for the experimental studies. The Rice Inspection Service, Grain Division, AMS, New Orleans, Louisiana, cooperates by providing assistance in grading rice samples from the research investigations. Cooperation has been initiated with the Western Division.

The Federal scientific effort at the Southern Division devoted to research in this area totals 2.7 professional man-years. The present effort is on chemical composition and physical properties.

PROGRAM OF STATE EXPERIMENT STATIONS

Rice research in progress at the State stations involves evaluation of new rice selections and varieties for agronomic and milling quality. Emphasis is placed upon developing and applying rapid, simple testing procedures useful for screening selections. Much of this work is carried out in cooperation with the Regional Rice Quality Laboratory. Laboratory methods for determining the quality of milled rice are sought for use in establishing objective standards for measurement of the quality of cooked rice. Cultural practices that may affect the quality, drying properties and storage stability of rice are evaluated to determine their influence upon processing characteristics and product quality.

Basic composition studies relate to the quantity and quality of the proteins, lipids and starch fractions and to their distribution within the kernels. Occurrence of mycotoxins in rice is being studied. Attempts to develop methods for the prevention and control of mycotoxin elaboration in rice during processing and marketing continue.

Product research involves development of effective ways to use rice in quantity food service. Another study seeks ways to make more efficient use of rice proteins through study of the supplementary value of high protein foods derived from rice and its by-products. The biological value of the proteins of rice, when used with multipurpose food is being investigated. This research is especially timely in view of the potential for use of rice in the diets of developing countries.

The influence of drying methods used on rough rice on the processing characteristics of rice is under study. Other variables such as maturity and variety are also studied.

The total State scientific effort devoted to utilization of rice is 1.9 professional man-years.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Investigation of the Distribution of Chemical Constituents in the Rice Kernel. In continued study of the distribution of the chemical constituents of the rice kernel, 12 consecutive peripheral layers of commercially milled Bluebonnet rice, totaling 19% of the kernel's weight, were removed by deep-milling in a prototype mill employing the tangential-abrasion principle. The protein, riboflavin, thiamine, niacin, phosphorus, and calcium contents of the flour decreased in the respective layers from the periphery toward the center. The level of each of these constituents in the outer layers greatly exceeded the level in the original kernel. The protein decreased from 22 to 12% in the 12 layers from periphery to center, but the amino acid pattern of the protein in the respective layers did not change, except for tryptophan,

which decreased by about 40% from layer 1 to layer 12. Although the total amount of protein present in the original and residual kernels differed by about 3%, the amino acid patterns of the proteins were identical. In comparison with wheat and corn proteins, these rice proteins contain the same or higher percentages of amino acids essential for nitrogen balance in adults, except for leucine, which is highest in corn.

The protein-rich rice flour holds promise in baby, geriatric, nonallergenic, and other dietary foods and in entirely new rice products. The residual kernels should be of special value for the manufacture of beer, wine, starch, and cosmetic preparations. Since wheat (hard winter and soft red), barley, and grain sorghum milled on a laboratory device showed high protein peripheral layers in all except soft red wheat, it appears that several products having greater nutritive value than the original grains may be prepared for human consumption, should deepmilling prove commercially feasible. (Sl 4-13).

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

Chemical Composition and Physical Properties

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Normand, F. L., Hogan, J. T., and Deobald, H. J. 1964. Improvement of culinary quality of freshly harvested rice by heat treatment. Rice J. 67(13), pp. 7-11.

Pominski, J., Schultz, E. Fred, Jr., and Spadaro, J. J. 1965. Effects of storage time after drying on laboratory milling yields of Southern rice. Rice J. 68(5), pp. 20-23, 43.

AREA NO. 15 - PEACH PROCESSING AND PRODUCTS

Problem. The peach industry in the Southeastern United States is dependent to a large extent on the fresh market. For example, in the South Atlantic States in 1962, 15,195,000 bushels of peaches were produced of which 12,237,000 bushels were sold on the fresh market; slightly less than 2,000,000 bushels were processed. A peach processing industry is needed in the Southeastern States to provide a profitable market for more of the edible peaches which do not meet fresh market standards and to rapidly convert a higher proportion of the overall crop to stable forms. Basic information, not now available, on the flavor components of peaches is needed to guide development of improved processed products from southern grown fruit.

Climatic conditions which favor rapid deterioration of fresh peaches both on and off the tree, erratic ripening periods and markets, and short lived peach orchards, are other factors contributing to the need for more extensively integrated fresh market-processing operations. There are technical problems preventing the more rapid development of the peach processing industry in the Southeastern States which must be overcome. Many of the peach varieties grown in the southeast require a modification of processing procedures to make satisfactory standard-type products. Still other varieties will not make standard-type products and new food forms must be found for them. Recent rapid advances in food science and processing technology make it possible through research to develop both new and improved peach products. These are needed to bolster the economics of the South's peach industry, as well as to provide the superior qualities, and greater convenience in food products, which the consumer now demands.

USDA AND COOPERATIVE PROGRAM

The Department has a program of basic and applied research on peaches being conducted under contract by the Georgia Agricultural Experiment Station, University of Georgia, Experiment, Georgia. Food chemists and food technologists conduct this research. Research to develop basic information on chemical composition and physical properties of peaches, particularly varieties grown in the Southeastern States, is in progress under one contract. Specifically, the objective of this research is to isolate, identify, and characterize the constituents of peach flavor and aroma, and acquire information needed to guide development of improved processed products from the fruit. Another contract, in the field of new and improved food products and processing technology, is concerned with research to develop optimum procedures for the production and preservation of puree and clear juice peach concentrates; to develop optimum procedures for the preparation and the handling under simulated commercial conditions of refrigerated fresh peach slices; to develop optimum procedures for canning Southeastern peaches; and to conduct experiments directed to the development of partially

dehydrated pasteurized peach products. Evaluation of different varieties of peaches, and of different processing variables are phases of the investigators. This research is carried out with the support of the Area Redevelopment Authority of the Department of Commerce.

The contract research involves a total level of effort of 2.0 professional man-years, 0.8 being on chemical composition and physical properties and 1.2 on new and improved food products and processing technology.

PROGRAM OF STATE EXPERIMENT STATIONS

The state stations did not report word in this area.

PROGRESS -- USDA AND COOPERATIVE PROGRAMS

A. Chemical Composition and Physical Properties

1. Basic Studies on Flavor and Odor Constituents of Peaches. A new project conducted under contract to the Georgia Agricultural Experiment Station is designed to develop basic information on flavor and odor constituents of peaches, lack of which had previously handicapped related research to impart optimum quality to new processed peach products. A large number of samples of Sullivan Elberta, Redglobe, Coronet, and Southland peaches have been frozen at various stages of maturity. Pits and peels have also been included. Samples of heated puree made from mixed varieties of peaches at soft ripe stage, samples of heated and unheated waste from the puree-finisher, and vapors trapped from the pulping machine and holding tank have also been collected. Other products prepared under the utilization contract (project SU-0-0-1(DC)) will be subjected to analyses of flavor and aroma.

In these four varieties of peaches, tannins (total tannin, leucoanthocyanin, and flavanols) appeared to decrease as the fruit matured through shipping ripe, firm ripe, and soft ripe stages. Within the same variety, the tannin content and the sensory evaluation of astringency were correlated, although this relationship was not demonstrable between varieties.

Peach volatiles have been shown to contain free fatty acids and carbonyl compounds. Removal of carbonyl compounds from peach flavor causes a marked change in the aroma, a result suggesting that these compounds affect flavor. When the volatile sulfur components of peaches were investigated, it was found that hydrogen sulfide was present in heated peaches; apparently the unheated peaches contained no volatile sulfur components. In a chromatographic analysis of the nonvolatile flavor components in soft ripe Sullivan Elberta peaches, the organic acids were shown to be mainly malic and citric acid, and the sugars mainly sucrose, fructose, and glucose. Thin-layer and gas-liquid chromatographic studies of peach samples before and after enzyme clarification indicate that pectin hydrolysis increases the recovery of volatile components. However, the possibility of an artifact has not yet been eliminated. Thin-layer chromatography has also been used to

demonstrate the presence of several free alcohols and aldehydes: ethanol, propanol, isoamyl alcohol, acetaldehyde, propionaldehyde, butyraldehyde, isovaleraldehyde, benzaldehyde. The findings reported will be checked through another season. (S3 2-44(C)).

B. New and Improved Food Products and Processing Technology

1. Development of New and Improved Processed Products from Southeastern Peaches. In other contract research, the Georgia Agricultural Experiment Station processed about 2000 bushels of peaches in its pilot plant during 1964 and is evaluating experimental packs of peach products. Clear peach juice concentrate. This product is already in commercial production, 4-1/2 million lbs. of B-grade peaches having been used to make 63° Brix for wine stock. It may also be useful in peach jelly, marmalade, waffle syrup, ice-cream, and fruit drinks. Puree-type peach concentrate. Puree was prepared from more than two dozen varieties, including peaches that ripened early, midseason, or late; that were clingstone, semi-cling, or freestone varieties; and that had poor, medium, or high flavor. Puree has been prepared from selected fruit for evaluation in ice-cream formulations. In addition, under supervision of GAES personnel, a commercial food processor reprocessed frozen puree to make a 2-fold puree-type peach drink, presently being test marketed by the Georgia Peach Commission. ERS and GAES are also conducting limited acceptance testing. To date, all evaluation is favorable. Chilled peach sections. In the 1964 season about 10,000 cases of jars of refrigerated fresh sliced peaches were prepared and successfully marketed. Firm ripe peaches with fully developed color made the best packs. The slices could be held in 30% syrup at 30° F. for more than two months, but preservatives did not increase the shelf-life. Two unsolved problems are the elimination of a "leafy" or benzaldehyde-type flavor and of the soft slick texture exhibited by some varieties. The commercial potential of the latter two products seems especially promising. Industry is exploring the feasibility of building a new plant or a plant addition to manufacture peach puree and refrigerated slices. Canned peaches. Peach halves were prepared from 17 varieties, with 4 sweeteners, and 8 cooking times. One variety each of early, mid, and late season fruit was processed in the shipping, firm-ripe, and soft-ripe stages. The packs are being allowed to equilibrate prior to evaluation. Drum-dried peach flakes. Preliminary tests have demonstrated that it is possible to make acceptable peach flakes from pulp-fortified peach puree. Additives such as sugar, starch, and a release agent improved the flakes, but the peach flavor is still weak. If such flakes can be produced economically, they may be useful in ice-cream, dry cereals, and similar products. Dehydrated peaches. Work on pasteurizing partially dehydrated peaches that had been blanched and vacuumized under 30% syrup containing half dextrose and half sucrose, with 0.1% ascorbic acid, was very encouraging. Twelve varieties and 71 lots were prepared for evaluation. Irradiated peaches. Irradiation pasteurization of peaches with 50,000 to 200,000 rad destroyed the chlorophyll and intensified the yellow and red color in the skin; greatly reduced peach flavor and aroma; and apparently intensified sourness, bitterness, and tartness. It did extend the shelf life of the fresh peaches from 4 to 10 days. (SU-0-0-1(DC)).

PUBLICATIONS -- USDA AND COOPERATIVE PROGRAMS

None

Line Project Check List - Reporting Year July 1, 1964 to June 30, 1965

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in Summary of Progress	Line Proj. Incl. in Area & Subheading
S1 4-	Rice Utilization Investigations-Southern Region			
S1 4-13	A study of the distribution of the constituents of rice in consecutive layers of the kernel and of the evaluation of selected fractions and degrees of milling, as a basis for the development of new and/or improved rice products.*	New Orleans, La.	Yes	14-A-1
S2 1-	Cotton Utilization Investigations			
S2 1-164 (Rev.)	Development of a prototype machine for removing short fibers from cotton.**	New Orleans, La.	Yes	3-A-3
S2 1-170 (C)	Investigation of the relationships between ease-of-care performance and the geometry of cotton fabrics.**	Dedham, Mass.	Yes	4-B-2
S2 1-178 (C)	Large-scale spinning evaluation of the effect of fiber properties and spinning variables on yarn properties and end breakage during spinning.**	Auburn, Ala.	Yes	2-A-1
S2 1-181 (Rev.)	Improvement in the bulk resilience and cohesion of cotton batts as a means of enhancing cotton's competitive position in this market.**	New Orleans, La.	Yes	5-E-3
S2 1-183 (C)	Investigation of the effects of mechanical treatments prior to, during, and following resin finishing on the ease-of-care properties of fabrics and garments.	Raleigh, N. C.	Yes	4-B-1
S2 1-193 (Rev.)	Development of stretchable-type cotton yarns and fabrics that will successfully compete with fabrics made from synthetic fibers and blends of synthetic fibers for clothing, household, and industrial uses.**	New Orleans, La.	Yes	5-E-1
S2 1-195	Investigation of radiochemical yields of high-energy radiation activated reactions of cotton to develop improved cotton products.	New Orleans, La.	Yes	1-B-2
S2 1-196	Fundamental study of mechanisms of cellulose etherifications.**	New Orleans, La.	Yes	1-B-3
S2 1-197 (C)(Rev.)	Evaluation of stretch-type cotton yarns in knit wear.	Raleigh, N. C.	Yes	5-E-1
S2 1-198	Relationship of fiber properties to fabric behavior in wash-wear treatments.**	New Orleans, La.	Yes	4-A-1
S2 1-199 (C)	Exploratory investigation of the reaction of acetylene and related compounds with cotton cellulose.**	Easton, Pa.	Yes	1-B-1
S2 1-200 (C)(Rev.)	Development of weather-resistant, water-repellent finishes for cotton.	Denton, Texas	Yes	5-A-1
S2 1-201	An investigation of the interfiber frictional force and associated fiber properties to improve the processing of cotton products.**	New Orleans, La.	Yes	1-A-5
S2 1-203	Investigation of the effects of time and environmental conditions on the rate of recovery of wash-wear cotton fabrics.**	New Orleans, La.	Yes	4-A-1
S2 1-204 (C)	The aerodynamic separation of lint cotton into individualized fibers to provide information needed for improving cotton textile processing equipment.	Westbury, L. I., N. Y.	Yes	3-A-4
S2 1-205 (C)	The development of cotton knit fabric having increased bulk, warmth, and dimensional stability.	Clemson, S. C.	Yes	5-E-1
S2 1-206 (C)	A determination of the structural components of the cotton fiber that contribute most to tensile strength and how they can be utilized to increase tensile and recovery properties to produce cotton products having enhanced physical properties.	South Pasadena, California	Yes	1-A-2
S2 1-207	Development of guides for the maximum utilization of cottons of varying fiber properties.	New Orleans, La.	Yes	2-A-1

* Initiated during reporting year.
** Discontinued during reporting year.

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in Summary of Progress	Area & Subheading
S2 1-208	Investigation of the effects of gross and fine structures of the cotton fibers on their physical behaviors.	New Orleans, La.	Yes	1-A-2
S2 1-209	Microscopical investigations of absorption phenomena			
S2 1-209 (Rev.)	in native, mercerized, and modified cottons.** *	New Orleans, La.	Yes	1-A-1
S2 1-210	The crosslinking of various physically modified crystalline forms of cotton as a means of producing resilient cotton textiles having improved appearance and durability to wearing.**	New Orleans, La.	Yes	1-B-1
S2 1-211	Investigation of finishing treatments to produce wash-wear cotton stretch fabrics with improved strength, drape, and hand.**	New Orleans, La.	Yes	4-C-1
S2 1-212	Development of test methods for stretch cotton textiles for use as a guide in producing better cotton stretch yarns and fabrics.**	New Orleans, La.	Yes	2-B-1
S2 1-213	The development by chemical and mechanical treatment of stretchable-cotton yarns suitable for weaving and knitting into fabrics with enhanced qualities.**	New Orleans, La.	Yes	5-E-1,2
S2 1-214	Separation and identification of the cleavage products of partially etherified cottons, including cross-linked cottons.	New Orleans, La.	Yes	1-A-4
S2 1-215	Development of an improved method of feeding the cotton card to produce higher quality textile products and thus increase the utilization of cotton.**	New Orleans, La.	Yes	3-A-2
S2 1-216	A study of reactions between epoxy compounds or their halohydrin precursors and cotton cellulose.	New Orleans, La.	Yes	1-B-1
S2 1-217 (C)	Effect of variation in structure on cotton fiber properties caused by environmental and genetic factors to obtain basic information important in optimum utilization of cotton.	College Station, Texas	Yes	1-A-2
S2 1-218	Development of improved instrumental techniques for selected elemental analysis of additively and chemically modified cottons to aid in improvement of cotton textile products.**	New Orleans, La.	Yes	1-A-4
S2 1-219	Improved methods of etherifying cotton cellulose.	New Orleans, La.	Yes	1-B-1
S2 1-220	Investigation of improved infrared spectral techniques for the study of modified cottons to aid in the development of textile products for specific end uses.**	New Orleans, La.	Yes	1-A-4
S2 1-221 (C)	Investigations to determine the effects of fiber extensibility on fiber breakage in mechanical processing.	Knoxville, Tennessee	Yes	1-A-3
S2 1-222 (C)	Treatment of cotton fibers by sonic energy to obtain basic information required for the development of improved equipment for processing cotton into textiles.	Carteret, N. J.	Yes	1-B-4
S2 1-223 (C)	Effect of the soiling environment on the soiling tendency of a series of cotton finishes.	Washington, D. C.	Yes	5-B-1
S2 1-224 (C)	Determination of optimum yarn constructions, knitting structures and prefabrication design for producing stretchable articles of knitted cotton wearing apparel by slack mercerization.	Raleigh, N. C.	Yes	5-E-2
S2 1-225 (C)	The relationship of molecular size, nature, shape, conformation, and configuration of organic non-aqueous compounds to their swelling power on cotton cellulose.	Brooklyn, N. Y.	Yes	1-A-1
S2 1-226	The development of cotton fabrics having improved warp and filling stretch properties by a comprehensive investigation of fabric and yarn structures and processing conditions during slack mercerization and resin treatment.	New Orleans, La.	Yes	5-E-2

*Initiated during reporting year.
**Discontinued during reporting year.

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in Summary of Progress	Area & Subheading
S2 1-227	Excellent smooth drying and wrinkle resistant fabrics by crosslinking cotton with highly reactive methylolamide amino acid derivatives.	New Orleans, La.	Yes	4-B-1
S2 1-228 (C)	Investigation of the physics of seam pucker in relation to fabric structure to develop improved sewing thread for wash-wear cotton products.	Atlanta, Ga.	Yes	4-C-2
S2 1-229 (C)	Development of a method for counting neps in cotton at various stages of textile processing.	South Pasadena, California	Yes	2-B-1
S2 1-230	Development of a durable wash-wear finish for cotton based upon monoalkyl carbamates.**	New Orleans, La.	Yes	4-B-1
S2 1-231 (C)	An investigation of the chemical modification of cotton through treatments with reagents in the vapor phase.	East Greenwich, Rhode Island	Yes	1-B-1
S2 1-232	The preparation of new finishing agents for cotton and cotton derivatives based upon lead and other metal compounds.	New Orleans, La.	Yes	1-B-1
S2 1-233	Preparation of fatty acid or hindered acid esters of cotton to form new or improved end-use textile products and investigation of reaction mechanisms involved.	New Orleans, La.	Yes	1-B-3
S2 1-234	Investigation of blending methodology to establish optimum blending procedures for maximum utilization of cottons differing widely in fiber properties.	New Orleans, La.	Yes	2-A-2
S2 1-235	Improvement of smooth drying properties, wet crease recovery, and moisture absorptivity in wash-wear cotton through swelling treatments.	New Orleans, La.	Yes	4-B-1
S2 1-237 (Gr)	Investigation of the configurational interactions between fibers and yarns in the region of local deformations in woven cotton cloth.	Cambridge, Massachusetts	Yes	1-A-5
S2 1-238 (Gr)	Correlation of surface microtopography of treated and untreated cotton fibers with resistance to soiling of cotton textiles.	Tucson, Ariz.	Yes	5-B-1
S2 1-239 (C)	Development of wash-wear cotton fabric with improved moisture absorptivity by use of reactive swelling agents.*	Birmingham, Alabama	Yes	4-A-2
S2 1-240 (Gr)	An exploratory study of the crosslinking of chemically modified cotton to obtain cotton fabrics with an optimum combination of resiliency and thermoplasticity.	Princeton, N.J.	Yes	1-B-1
S2 1-241 (C)	Investigation of factors influencing comfort in cotton apparel fabrics.	Washington, D. C.	Yes	1-A-6
S2 1-242 (C)	To determine optimum processing procedures for cotton differing in tensile and elastic properties and relate these properties to mechanical processing performance, yarn, and fabric properties.*	Auburn, Ala.	Yes	2-A-2
S2 1-243 (C)	Development of finishes for cotton fabrics to render them more rapid drying.*	Washington, D. C.	No	
S2 1-245 (C)	The development of weather resistant cotton textiles with improved physical properties by interfacial and graft polymerization.	Birmingham, Ala.	Yes	5-A-1
S2 1-247	An investigation of the chemical modification of cotton fabrics using reagents in the form of fogs or aerosols.	New Orleans, La.	Yes	1-B-1
S2 1-248 (Gr)	Elucidation of the role of fiber morphology on frictional behavior important in mechanical processing of cotton fibers and in the behaviors of cotton products.*	Atlanta, Ga.	Yes	1-A-5
S2 1-249	Investigations of cotton fiber-property changes, during mechanical and chemical processes, which are responsible for altered sorption of alkali solution.*	New Orleans, La.	Yes	1-A-1

* Initiated during reporting year.
** Discontinued during reporting year.

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in Summary of Progress	Area & Subheading
S2 1-250	Treatment of cotton with fluorochemicals to produce a finish with low surface energy.	New Orleans, La.	Yes	5-B-2
S2 1-251	Exploratory research to impart multifunctional properties to cotton through the use of specially tailored compounds.	New Orleans, La.	Yes	5-C-1
S2 1-252	Development and evaluation of a new machine for opening and blending bales of cotton in any desired proportion in textile mills.	New Orleans, La.	Yes	3-A-1
S2 1-253	Wash-wear cottons of high abrasion resistance by the application of durable polymeric coatings.	New Orleans, La.	Yes	4-B-1
S2 1-254	Development of optimal cotton fabric structures for men's trousers and dress suits.	New Orleans, La.	Yes	4-B-2
S2 1-255	Investigation of effective crosslinks in cotton modified by chemical treatment.	New Orleans, La.	Yes	1-A-4
S2 1-256	Development of multipurpose finishes for outdoor cotton fabrics with improved physical properties.	New Orleans, La.	Yes	5-A-1
S2 1-257	Development of durable inexpensive flame retardants for cotton.*	New Orleans, La.	Yes	5-C-1
S2 1-258	Exploratory investigation of reversible chemical reactions to obtain information basic to the development of a commercially feasible reversible crosslink.	New Orleans, La.	Yes	1-B-1
S2 1-259	The fixation of antimicrobial agents in cotton fabric by use of zirconium compounds, to impart improved weather resistance.*	New Orleans, La.	Yes	5-A-1
S2 1-260	Investigation of resistance to edge abrasion in wash-wear cotton and methods for improvement.*	New Orleans, La.	Yes	4-A-2
S2 1-261	Investigation of spatial and structural effects of reversible and conventional crosslinks in cotton.*	New Orleans, La.	Yes	1-B-1
S2 1-262	An investigation of tensile and torsional or bending recoveries of single fibers, yarns, and fabrics of wash-wear treated cottons under wet and dry conditions.*	New Orleans, La.	Yes	4-A-1
S2 1-263	Microscopical investigations of chemical substitution and crosslink formation in cotton, to provide information basic to research required for increased utilization of cotton.*	New Orleans, La.	Yes	1-A-2
S2 1-264	Investigation of the fluorescence spectra of native and modified cottons, to obtain information needed in the development of improved textile products.*	New Orleans, La.	Yes	1-A-4
S2 1-266 (C)	Development of a research instrument for accurately and automatically determining length, length distribution and diameter of cotton fibers.*	South Pasadena, California	No	
S2 1-267	Wash-wear fabrics of increased strength, durability, and luster by crosslinking fabrics woven of premercerized yarns.*	New Orleans, La.	Yes	5-D-1
S2 1-268	Development of new basic information concerning the reactions of cellulose by use of nuclear magnetic resonance and other spectroscopic techniques to facilitate research in the chemical modification of cotton.*	New Orleans, La.	Yes	1-A-4
S2 1-269	Investigations to improve the production and the performance characteristics of chemically treated cotton batting.*	New Orleans, La.	Yes	5-E-3
S2 1-270	Investigation of the formation of free radicals in fibrous cotton cellulose and the reaction mechanisms of the activated cellulose with selected reagents, to develop new and improved cotton products.*	New Orleans, La.	Yes	1-B-2
S2 1-271	Development of improved insect-proof cotton bags for the storage and shipment of food commodities, to maintain and expand markets for cotton.*	New Orleans, La.	Yes	5-F-1

* Initiated during reporting year.

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in Summary of Progress	Line Proj. Incl. in Area & Subheading
S2 1-272	The relation of fiber properties to fabric behavior in chemically treated cotton fabrics.*	New Orleans, La.	Yes	4-A-1
S2 1-273	Development of a method for removing short fibers and improving fiber parallelization at textile carding machines.*	New Orleans, La.	Yes	3-A-3
S2 1-274	The effect of high production carding on fiber length distribution and formation of fiber hooks in cotton.*	New Orleans, La.	Yes	2-A-2
S2 1-275	Development of more reliable methods of appraising damage done by abrasive action on all cotton wash-wear fabrics.*	New Orleans, La.	Yes	2-B-1
S2 1-276	Investigation of new and improved x-ray diffraction techniques for the study of the crystalline structure of cotton and chemically modified cotton in contact with various interacting liquids.*	New Orleans, La.	Yes	1-A-4
S2 1-277	Investigation of the chemical kinetics of cellulose etherifications to expand utilization of cotton.*	New Orleans, La.	No	
S2 1-278	Fundamental investigation of basic actions in cotton textile processing by means of high speed photography.*	New Orleans, La.	No	
S2 1-279	Development and evaluation of prototype equipment for feeding cotton to textile cards to produce cotton products with improved physical properties.*	New Orleans, La.	No	
S3 2-	Citrus and Other Fruit Utilization Investigations - Southern Region			
S3 2-34 (Rev.)	Investigation of the biochemical mechanism of the conversion of precursors to carotenoids in grapefruit as a basis for improvement of processing characteristics of and products from colored grapefruit.**	Weslaco, Texas	Yes	9-A-4
S3 2-38 (Rev.)	Investigation of the chemical and physical nature of components of cloud of orange juice, to provide better understanding and control of factors affecting stability of orange juice products.**	Winter Haven, Fla.	Yes	9-A-3
S3 2-39 (C)(Rev.)	Investigation of the effect of maturity of grapefruit on total flavonoids, naringin, and poncirin; and on the chemistry, and nature of naringin and naringin-derived compounds to provide a scientific basis for the control of bitterness in processed grapefruit products.	Norman, Okla.	Yes	9-A-2
S3 2-40	Utilization of natural and debittered grapefruit juice and puree as bases for the development of improved fruit juice blends, drinks, and concentrates.**	Weslaco, Texas	Yes	9-B-1
S3 2-41	Investigations on the foam-mat drying of concentrated grapefruit juices to provide a new grapefruit product of optimum flavor and high stability.**	Winter Haven, Fla.	Yes	9-C-1
S3 2-42	Investigations of the identities, quantities and chemistry of components in Florida grapefruit responsible for excessive bitterness and harshness in processed products.**	Winter Haven, Fla.	Yes	9-A-2
S3 2-43	Investigations on conditions for drying as related to the storage stability and quality of "foam-mat" dried citrus products.	Winter Haven, Fla.	Yes	9-C-1
S3 2-44 (C)	Composition of flavor components of peaches (with emphasis on existing commercial varieties in the Southeastern United States).	Experiment and Athens, Ga.	Yes	15-A-1

* Initiated during reporting year.
** Discontinued during reporting year.

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in Summary of Progress	Area & Subheading
S3 2-46 (C)	Development of practical and efficient pilot plant process for the manufacture of enzymatically debittered grapefruit juice and products with improved flavor, product stability, and storage characteristics.	Lake Alfred, Fla.	Yes	9-C-2
S3 2-47	Identification of recently isolated flavones and other neutral orange peel constituents and evaluation of their relation to bitterness and harshness in orange products.*	Winter Haven, Fla.	Yes	9-A-2
S3 2-48	Study of the composition of essential oils in citrus products, particularly orange, to provide a basis for improvement in quality and uniformity of citrus products.*	Winter Haven, Fla.	Yes	9-A-1
S3 2-49	Processed grapefruit products of greater attractiveness to the consumer through exploration of means to prevent or minimize the formation of bitter components in the fruit.*	Winter Haven, Fla.	Yes	9-A-2
S3 2-50	A study of off-flavor development in processed citrus juice in relation to the lipid composition of the suspended matter.*	Winter Haven, Fla.	No	
S3 5-	Sweetpotatoes, Cucumbers, and Other Vegetable Utilization Investigations - Southern Region			
S3 5-21	Investigation of the flavor and aroma components in natural and pure culture fermented cucumber pickle products.**	Raleigh, N. C.	Yes	10-A-1
S3 5-22	Investigation to develop new and improved processed products from Southern-grown vegetables other than sweetpotatoes and celery, including cooperative studies with federal, state, and industry agencies.	Weslaco, Texas and Raleigh, N. C.	Yes	10-B-3 10-C-2
S3 5-23 S3 5-23 (Rev.)	Application of new basic information on the chemical constituents of celery stalk (petiole) to the development of processed products of improved flavor and convenience.** *	Winter Haven, Fla.	Yes	10-B-2
S3 5-24 (Gr)	Elucidation of molecular structure and chemical characteristics of the pectinase inhibitor in sericea forage and other plant sources.*	Durham, N. C.	Yes	10-A-2
S3 5-25	Development of processing innovations for manufacture of stable, precooked, dehydrated sweetpotato flakes from roots of different varieties and environmental history.	New Orleans, La.	Yes	10-B-1 10-C-1
S3 5-27	Adaptation of laboratory pure culture fermentation procedures to a commercially feasible process for the manufacture of pickled vegetable products.	Raleigh, N. C.	Yes	10-C-2
S3 5-28	Investigations of the chemistry and biochemistry of the carotenoid pigments in fruits and vegetables to facilitate the development of improved and more attractive processed products.*	Raleigh, N. C.	Yes	10-A-3
S3 5-29	Investigation of effects of cucumber substrate, bacterial species and other environmental factors on the flavor and aroma of cucumbers and fermented cucumber products.*	Raleigh, N. C.	No	

* Initiated during reporting year.
** Discontinued during reporting year.

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in Summary of Progress	Line Proj. Incl. in Area & Subheading
S4 1-	Cottonseed, Peanut and Other Oilseed Investigations - Southern Region			
S4 1-89 (C)	Polymerization of vegetable oil, pine gum, and sugarcane derivatives and evaluation of properties of the polymers for use as elastomers, plastics, thickening agents, and protective coatings.	Tucson, Arizona	Yes	6-D-1 11-B-3
S4 1-102 (Rev.)	Development of hydrogenation techniques for cottonseed oil which will reduce cyclopropenoids with the least possible isomerization of the other unsaturated fatty acid groups.**	New Orleans, La.	No	
S4 1-103 (C)	Investigations of gossypol esters and of mild oxidation products of gossypol and gossypol derivatives to develop information needed to aid the production of cottonseed meals and oils of the highest quality.	Knoxville, Tenn.	Yes	6-A-2
S4 1-104 (C)	Investigation of the chemical and physical properties of cyclopropene fatty acids in cottonseed.**	Urbana, Illinois	Yes	6-A-3
S4 1-105	Investigations on the cyclopropene acid constituents in cottonseed and cottonseed products.**	New Orleans, La.	Yes	6-A-3
S4 1-106 (C)	Investigation of the flavor and aroma components in processed peanut products.	New York, N. Y.	Yes	7-A-2
S4 1-107 (C)	Chemical investigations of cyclopropenoids to develop means of eliminating or physiologically inactivating the cyclopropenoids found in cottonseed products.	Urbana, Illinois	Yes	6-B-2
S4 1-109	Investigation of the proteins and nonglyceride lipid-soluble constituents of peanuts and processed peanut products to expand their utilization.**	New Orleans, La.	Yes	7-A-2
S4 1-109 (Rev.)	Investigations of the phospholipid, plasmalogen, and other lipid or lipid-soluble constituents of peanuts and processed peanut products to expand the utilization of food grade peanuts.*	New Orleans, La.	No	
S4 1-110	Investigations to isolate and identify the factors in cottonseed meal that cause mortalities among swine to develop information for producing cottonseed meals that can be used without restriction in feeding to any nonruminants.**	New Orleans, La.	Yes	6-C-1
S4 1-112 (C)	Investigations of chemical transformations of fat and terpene olefinic compounds by hydroboration and suitable subsequent reactions to produce useful products.	Lafayette, Ind.	Yes	6-A-3 11-A-1
S4 1-113	The development of exterior and interior intumescing, fire-retardant coatings based on tung oil and tung oil derivatives.	New Orleans, La.	Yes	8-B-1
S4 1-114	Development of methods for upgrading the quality of cottonseed oil by improving the color and eliminating undesirable components such as cyclopropene acids.	New Orleans, La.	Yes	6-B-2
S4 1-115 (C)	Ethylene copolymerization with unsaturated fatty acid and gum naval stores compounds to extend the industrial utilization of agricultural products in commercial plastics.	Tuscola, Ill.	Yes	6-D-1 11-B-3
S4 1-116	Isolation, identification, evaluation, and control of fungi and toxic fungal metabolites which may develop during processing of cottonseed and peanuts to improve the acceptance of their processed products.	New Orleans, La.	Yes	6-A-4 7-A-3
S4 1-117 (C)	Development of practical processing methods for inactivation of cyclopropene groups in cottonseed meal that decrease its value as a feed for laying hens.	Chicago, Ill.	Yes	6-C-2

* Initiated during reporting year.
** Discontinued during reporting year.

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in Summary of Progress	Area & Subheading
S4 1-118 (C)	Development of peanut products for use in preparation and fortification of processed and convenience foods to extend usefulness of peanuts.*	Auburn, Ill.	Yes	7-B-2
S4 1-119 (C)	A study of the relation of the carbohydrate, amino acid and protein components of the peanut to the formation of flavor and aroma during roasting, with the objective of expanding the direct utilization of this commodity.	Stillwater, Okla.	Yes	7-A-2
S4 1-120 (C)	Development of processing methods using peanuts of known history with respect to different growing, harvesting, and curing conditions that will provide processed peanut products of high quality and free of mycotoxins.	College Station, Texas	Yes	7-A-3
S4 1-121 (C)	Study of the limiting environmental conditions for the elaboration of mycotoxins in peanuts to develop information needed to assure the processing of highest quality peanuts.	Auburn, Ala.	Yes	7-A-3
S4 1-123	Study of rates of extraction of cottonseed with acetone-hexane-water solvent mixtures and nature and quantities of constituents in miscellas and rheological properties of marcs, to develop information basic to the production of cottonseed meal and oil of the highest quality.	New Orleans, La.	Yes	6-C-2
S4 1-124	Preparation and evaluation of N-disubstituted fatty amides considered potentially useful as plasticizers, nitrile rubber softeners, and antifungal agents, to develop information basic to the increased utilization of cottonseed and other seed oils assigned to SU.	New Orleans, La.	Yes	6-D-1
S4 1-125	Improvement of processes for making cocoa butter-like fats from cottonseed and peanut oils and the development of data and processing techniques for improving the performance of confectionery fats.*	New Orleans, La.	Yes	6-B-1
S4 1-126	Development of low-fat peanuts having acceptable peanut flavor and texture characteristics.*	New Orleans, La.	Yes	7-B-2
S4 1-127	Investigation to determine processing conditions for the production of oils and meals of maximum quality from glandless cottonseed.*	New Orleans, La.	Yes	6-C-2
S4 1-128	Development of new and improved techniques for preparing useful derivatives of cottonseed and peanut oils by esterification and interesterification.*	New Orleans, La.	Yes	6-B-1
S4 1-129	Investigation of methods for correlating and predicting solubilities of homologous and analogous long chain saturated and unsaturated fatty acid derivatives.*	New Orleans, La.	Yes	6-A-3
S4 1-130	Investigation of the chemical composition and characteristics of the protein systems of cottonseed to serve as a basis for improvement of nutritive value of cottonseed meal and flour.*	New Orleans, La.	Yes	6-C-1
S4 1-132 (C)	Study of sterilizing or inactivating treatments in conjunction with artificial drying and curing of peanuts to develop processing conditions needed for producing mycotoxin-free roasted peanut products of optimum quality.*	Stillwater, Okla.	No	
S4 1-134 (Gr)	The development of procedures for synthesizing labeled malvalic acid esters.*	Boston, Mass.	No	

* Initiated during reporting year.

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in Summary of Progress	Area & Subheading
S5 1-	Sugars and Sirups Investigations - Southern Region			
S5 1-77	Chemical and physical investigations of sugar refining operations to improve processing of cane sugar.	New Orleans, La.	Yes	12-A-1
S5 1-80	Pilot plant development of improved methods of purification of juices and sirups to increase sugar recovery and reduce costs of processing sugarcane.* **	New Orleans, Houma, and Baton Rouge, La.	Yes	12-B-1
S5 1-81	Investigation of extractable complex polysaccharides of sugarcane in relation to efficiency of recovery and purification of sugar.* **	New Orleans and Houma, La.	Yes	12-A-1
S5 2-	Naval Stores Investigations - Southern Region			
S5 2-38	Preparation of chemical intermediates from pine gum products for use in the preparation of new synthetic polymers, plastics and resins to expand the utilization of turpentine and rosin.**	Olustee, Fla.	Yes	11-B-1
S5 2-39 (Rev.)	Development of a method for the determination of rosin and rosin derivatives in protective coatings.	Olustee, Fla.	Yes	11-B-3
S5 2-44	Hypochlorite modification of rosin and resin acids for use as chemical intermediate for preparation of new industrial resins, surface coatings, plastics, rosin soap emulsifiers and similar materials.**	Olustee, Fla.	Yes	11-B-1
S5 2-45 (C)	Application of the oxo and related reactions to terpenes and resin acids to produce alcohols, aldehydes, and/or acids and characterization of the products thus obtained.	Cincinnati, Ohio	Yes	11-B-3
S5 2-46 (C)	Synthesis of terpene alcohols and glycols for use in the production of new and useful terpene derived polymers.	Ithaca, N. Y.	Yes	11-B-3
S5 2-47	The utilization of photosensitized oxidized pine gum and components in the fields of plastics and rubber.**	Olustee, Fla.	Yes	11-B-2
S5 2-48	Reaction of terpenes derived from turpentine with dienophiles to produce useful acids, aldehydes, amines, nitriles, sulfones, and related derivatives.	Olustee, Fla.	Yes	11-B-1
S5 2-49 (C)	Investigation of the acid-catalyzed dimerization of alpha-pinene.	Gainesville, Fla.	Yes	11-B-1
S5 2-51	Development of practical methods for preparing the levopimaric acid-formaldehyde adduct, and the evaluation of this and selected derived products for industrial uses.*	Olustee, Fla.	Yes	11-B-1
S5 2-52	The preparation and reactions of epoxides and ozonization products of resin acids and their derivatives, to explore potential new industrial uses.*	Olustee, Fla.	Yes	11-B-3
S5 2-53	Development of improved polyester resins from resin acids.*	Olustee, Fla.	Yes	11-B-3
S5 2-55	The preparation of polymerizable monomers for vinyl and condensation-type polymers from terpene acids and terpene acid derivatives.*	Olustee, Fla.	Yes	11-B-1
S5 5-	New and Replacement Crops Utilization Investigations - Southern Region			
S5 5-51	Investigations of the chemical characteristics of new sweet sorghum canes which determine their suitability for sugar recovery.*	Weslaco, Texas	Yes	13-A-1

* Initiated during reporting year.
** Discontinued during reporting year.

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in Summary of Progress	Line Proj. Incl. in Area & Subheading
S5 5-52	Preparation of chemically modified fatty acids or oils, from the potential new oilseed crops Cuphea, Limnanthes, and members of the Umbelliferae, suitable for evaluation as corrosion inhibitors, biologically active compounds, in plastics, or other industrial products.* **	New Orleans, La.	Yes	13-B-1
SU-0-0-1 (DC)	Development of new and improved processed peach products, with special emphasis on the suitability of existing commercial varieties in the Southeast for the production of fresh peach concentrates.	Experiment, Ga.	Yes	15-B-1
SU-0-0-2 (SG)	Improvement of fat emulsions suitable for use in intravenous alimentation.	New Orleans, La.	Yes	6-B-1
SU-0-0-3 (AID)	A study of the preparation of cottonseed and peanut flours and their derived products for human consumption in developing countries.*	New Orleans, La.	Yes	6-B-3 7-B-1
SU P 1	Seed Protein Pioneering Research Laboratory.***	New Orleans, La.	Yes	7-A-1
SU P 2	Plant Fibers Pioneering Research Laboratory.***	New Orleans, La.	Yes	1-A-4
UR-A7-(40)-3	A study of the relationship of substituent fatty acid groups on the physical properties of diacid triglycerides of palmitic and stearic acids as a means of increasing the utilization of cottonseed oil for food and industrial purposes.	Bombay, India	Yes	6-A-3
UR-A7-(20)-4	Investigation of the photochemical degradation of cotton to derive information which would enhance the utilization of cotton.	Bombay, India	Yes	1-A-3
UR-A7-(40)-12	Effect of heat on tung oil and derivatives of tung oil and characterization and identification of compounds resulting from heat treatments, to extend the utilization of tung oil.	Poona, India	Yes	8-A-2
UR-A7-(20)-19	A study of the relation between fine structure and mechanical properties of cotton fibers by swelling and stretching treatments, as a means of improving the properties, and thereby increasing the utilization of cotton.	Ahmedabad, India	Yes	1-A-4
UR-A7-(40)-26	Studies of the addition of carbenes to unsaturated fatty materials derived from cottonseed oil, to provide possible new outlets for the utilization of cottonseed oil.	Bangalore, India	No	
UR-A7-(40)-28	Investigation of the synthesis and properties of new-type glycol monoalkyl ethers for the control of water evaporation, to extend the industrial utilization of cottonseed oil.	Poona, India	No	
UR-A7-(20)-30	Investigation of new solvents for molecular weight determination of cellulose, to obtain basic information needed to improve cotton products and thereby enhance the utilization of cotton.	Bombay, India	Yes	1-A-3
UR-A7-(20)-32	Investigation of the microbial decomposition of cellulose with special reference to the effect of Indian bacterial organisms on cotton and cotton fabrics to provide basic information for the improvement of cotton products.	Bombay, India	No	

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** Discontinued during reporting year.
*** There are no line projects under this work project.

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in Summary of Progress	Line Proj. Incl. in Area & Subheading
UR-A7-(20)-33	Investigations of the preparation of radioresistant and radiosensitive celluloses to obtain basic information needed for useful applications of high energy radiation in cotton textile processing, thereby enhancing the utilization of cotton.	Bombay, India	No	
UR-A7-(20)-46	A study of the physical chemistry and thermodynamics of solution and vapor phase adsorption on and in the cotton fiber to obtain basic information needed to improve cotton processing and utilization.	Ahmedabad, India	No	
UR-A7-(20)-51	Investigation of means to minimize fiber hooked ends in cotton card and drawing slivers to develop processing organizations of optimum efficiency, and thus to promote increased utilization of cotton.	Ahmedabad, India	Yes	2-A-2
UR-A7-(20)-59	An investigation of moisture sorption and desorption by crosslinked cotton celluloses over the entire humidity range, in relation to the state of swelling under which the cellulose is crosslinked and to other properties of the crosslinked celluloses, to obtain basic information of value in increasing the textile uses of cotton.*	Delhi, India	No	
UR-A7-(20)-84	An investigation of heat and mass transfer rates and other basic engineering concepts as related to the drying and curing of resin-treated cotton textiles by counter-current solid-gas contact systems, to obtain fundamental information necessary to devise more efficient textile processing techniques, thereby increasing the utilization of cotton in textile applications.*	Delhi, India	No	
UR-A7-(20)-85	An investigation to determine the factors that affect the drafting capacity, optimum conditions, spinning efficiency, and yarn quality of the direct sliver spinning system to provide information needed to improve cotton processing and increase the utilization of cotton products.*	Ahmedabad, India	No	
UR-A10-(20)-5	Fundamental investigation of crimp in cotton fibers and its relationship to other fiber properties, as well as its effect on processing performance and product quality.**	Jerusalem, Israel	Yes	1-A-5
UR-A10-(40)-34	Investigation of π-complexed organometallic compounds derived from polyunsaturated fatty acids, to obtain fundamental information needed in expanding the utilization of cottonseed oil.	Haifa, Israel	No	
UR-A10-(20)-50	A fundamental study of the oxidation of cotton and crosslinked cotton by hypochlorite, hypobromite, and other oxidizing agents, to obtain information needed on the kinetics of the oxidation and the changes in physical and chemical properties, in order to improve the characteristics of cotton for various end uses.	Jerusalem, Israel	Yes	1-B-3
UR-A10-(40)-53	A study of the preparation of new chemical derivatives from acrylonitrile and fatty acids derived from the oils of cottonseed, tung, parsley seed, Limnanthes douglasii, Cuphea, and other oilseeds of the southern region of the United States to obtain information leading to potential new uses for these oils.*	Jerusalem, Israel	No	

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** Discontinued during reporting year.

Work & Line Project Number	Work and Line Project Titles	Work Locations During Past Year	Line Proj. Incl. in Summary of Progress	Line Proj. Incl. in Area & Subheading
UR-A10-(40)-54	An investigation of metalation reactions employing alkali and alkaline earth metals and their derivatives for the modification of mono- and dienoic fatty acids to provide increased functionality, thereby leading to possible new uses for cottonseed, Limnanthes douglasii, and umbelliferous oils in industrial applications.*	Jerusalem, Israel	No	
UR-A10-(20)-56	The synthesis and determination of the properties of new aziridinyl phosphorus compounds having potential for use in the treatment of cotton to afford new products of increased utility.*	Jerusalem, Israel	No	
UR-A11-(50)-7	Isolation and identification of the nucleic acid derivatives of cane molasses, in order to obtain information applicable to expanding the utilization of molasses industrially and in feeds.	Kyoto, Japan	Yes	12-A-1
UR-E4-(20)-1	A fundamental study of the nature and origin of reversals in cotton fibers, and of their relation to mechanical properties of these fibers, to obtain information needed in the development of improved cotton products.*	Ghent, Belgium	No	
UR-E9-(20)-61	A fundamental study of the relation of crystallinity to accessibility in native and modified cotton, to obtain information on the supermolecular structure of cotton that is needed in the development of improved cotton products.	Paris, France	Yes	1-A-4
UR-E10-(20)-2	Development of an apparatus for counting neps in cotton card web as an aid toward increasing the quality of cotton products.	Reutlingen-Stuttgart, West Germany	Yes	2-B-1
UR-E15-(40)-33	Investigations on the physical and physicochemical properties of cottonseed proteins, to obtain basic information needed for the increased utilization of cottonseed.	Rome, Italy	Yes	6-A-1
UR-E15-(40)-35	A study of the mechanism of gossypol toxicity counteraction by L-lysine to gain information needed to permit the increased use of cottonseed products in animal feeds.	Milan, Italy	No	
UR-E15-(40)-44	Experimental studies to elucidate the role of cottonseed meal in the induction of hepatoma in rainbow trout to obtain fundamental information concerning the suitability of cottonseed meal for use in rations for this species.*	Aosta, Italy	No	
UR-E19-(20)-4	A fundamental study of the role of the structural elements of the cotton fiber in response to stress in deformation and recovery, to obtain information needed in the development of improved cotton products.	Delft, Holland	Yes	1-A-2
UR-E19-(20)-12	An investigation of the fundamental mechanisms and bonding forces that could be used to improve the tensile strength and other physical properties of cotton textiles, as a means of increasing the utilization of cotton.	Delft, Holland	Yes	1-A-2
UR-E21-(20)-27	An investigation of the mathematical and theoretical aspects of the relationship between the fiber length distribution of cotton specimens before and after sample preparation to obtain basic information needed to improve cotton processing.*	Lodz, Poland	No	
UR-E25-(20)-2	Determination of relationship between the cohesion of cotton fibers and other physical properties of fibers, rovings, and yarns, as a step in improving product quality and processing efficiency.**	Barcelona, Spain	Yes	2-A-1

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** Discontinued during reporting year.

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UR-E25-(20)-13	Determination of effect of drafting forces in high-draft systems on uniformity and strength of cotton yarns as a step in improving product quality and processing efficiency.**	Barcelona, Spain	Yes	2-A-2
UR-E25-(20)-31	A study of the measurement of the "total hairiness" of cotton yarn and the determination of the mechanical factors contributing toward its formation, to obtain basic information needed to improve the processing of cotton into textiles.	Barcelona, Spain	Yes	1-A-5
UR-E25-(50)-36	Development of new or improved methods of synthesizing, isolating, and purifying selected terpene alcohols for use as standards, to obtain basic information on the composition and properties of products made from pine gum as an aid in developing new industrial uses for naval stores products.	Barcelona, Spain	No	
UR-E26-(20)-1	Investigation of the mechanism of crease formation and recovery in ease-of-care treated cotton fabrics to supply fundamental knowledge required for the design of improved textiles, thereby increasing the utilization of cotton.*	Gothenburg, Sweden	No	
UR-E26-(20)-2	Fundamental investigation of setting reactions for cotton fabrics and garments, to develop information basic to the improvement of cotton products, thereby increasing the utilization of cotton.	Gothenburg, Sweden	Yes	1-A-2
UR-E26-(20)-6	Basic investigation of the behavior of cotton subjected to aerodynamic forces, for the purpose of improving the processing characteristics of cotton textiles.	Gothenburg, Sweden	Yes	1-B-4
UR-E27-(20)-2	A study of the chemistry and structural nature of the bonds formed between formaldehyde and cellulose in formaldehyde-treated cottons to provide basic information needed to improve the utility of the cotton fabrics.	Zurich, Switzerland	No	
UR-E29-(40)-26	Studies on the fatty acid and glyceride composition of cottonseed oil and the crystallizing behavior of some of the major components, to obtain fundamental information that will contribute to the development of improved edible products and hence to expanded utilization of cottonseed oil.	Leatherhead, Surrey, England	Yes	6-A-3
UR-E29-(20)-55	A fundamental study of the preparation and properties of phosphazene (Phosphonitrilic) and phosphoryl chloride derivatives having potential for reaction with cotton cellulose, to obtain information needed in the development of new useful products from cotton, thus increasing its utilization.	London, England	Yes	1-B-1
UR-E29-(20)-65	A study of the effect of caustic soda and other swelling agents on the fine structure of cotton, to obtain basic information needed to improve cotton products and thereby enhance the utilization of cotton.	Manchester, England	Yes	1-A-4
UR-E29-(20)-78	Investigation of chemical modifications of cotton fabrics involving control of lateral molecular order and distribution of crosslinks, to provide basic information needed to improve the performance characteristics of cotton fabrics as a means of increasing their utilization.*	Manchester, England	No	
UR-01-(40)-2	An investigation of the chemistry and biological effects of cyclopropenoid compounds that occur in cottonseed and cottonseed products, to obtain basic information needed to improve the utilization of these commodities.	Ryde, New South Wales, Australia	Yes	6-A-3

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** Discontinued during reporting year.

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UR-S9-(40)-2	Preparation, characterization, and evaluation of derivatives of gossypol from cottonseed for use as biologically active materials, ultraviolet adsorbers and other valuable products.	Montevideo, Uruguay	Yes	6-D-1